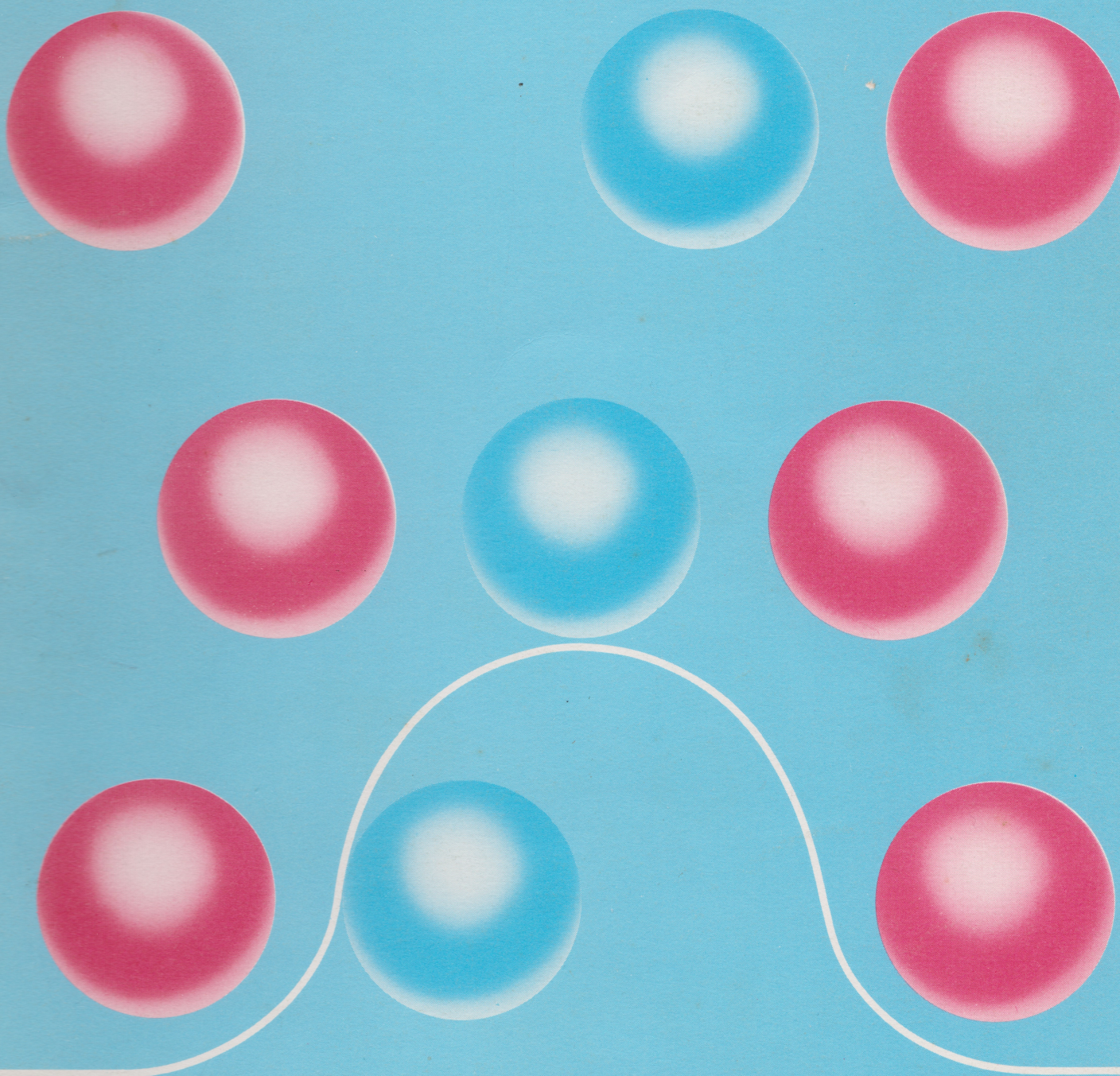




Chemical reactions





The Open University

Science Foundation Course Units 11 and 12

CHEMICAL REACTIONS

Prepared by the Science Foundation Course Team

THE OPEN UNIVERSITY PRESS

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Preamble

Units 11 and 12 deal with rates and equilibria of chemical reactions. The division between the Units is rather arbitrary; the more logical breaks are probably after sections 11.3.3 and 12.1.2.

We suggest that the most useful time to do the Home Experiment for Unit 11 is after you have completed section 11.4.1. In any case, it would be advisable to complete it before starting section 11.4.2, as you will be able to use your own results from there on. You should also read section 11.4.1 before starting the experiment. We suggest that you do the Home Experiment for Unit 12 after completing the Unit.

The material in the text is expressed mainly in general terms. We have used the broadcast media for Unit 12 to treat some specific examples. The television programme of Unit 11 will deal with the theoretical ideas developed up to the end of section 11.2, and the television programme for Unit 12 will deal with some methods of obtaining the type of information discussed in section 11.4. The radio programme for Unit 12 will discuss the problem of using the information discussed in the two Units to determine suitable conditions for industrial scale production.

We have made the aims and objectives and Table A combined lists covering both Units, and collected the *SAQs* after Unit 12.

Aims

To examine some of the factors that determine the rates and equilibria of chemical reactions. In Unit 11 this will be based on a theoretical study of very simple reactions and in Unit 12 on experimental information referring to the concepts developed in Unit 11.

Objectives

After you have completed your study of these Units, you should be able to:

1 Define, or recognize, adequate definitions of, or distinguish between, true and false statements concerning each of the terms, concepts and principles in column 3 of Table A, except those terms in brackets.

Unit 11

2 Given the value of the heat of a reaction, decide whether the reaction is exothermic or endothermic.

3 Given the various bond dissociation energies involved in a simple reaction, calculate the enthalpy change for the reaction.

4 Distinguish between the enthalpy change for a reaction and the activation energy of the reaction by drawing a graph.

5 On a similar graph, indicate the meaning of activated complex.

6 Sketch (or select the correct sketch of) a reaction co-ordinate for a simple reaction of given thermicity.

7 Describe in qualitative terms how the energy can be obtained for thermal reactions.

8 Sketch the Boltzmann distribution and indicate how it changes with temperature.

9 Relate the changes in the Boltzmann distribution to the way rates of reactions vary with temperature.

10 Sketch (or select a correct sketch of) the variation of concentration with time for reactants and products in a reaction.

11 Define the rate of a reaction.

12 Relate the rate of a reaction to a plot of concentration against time.

13 Given the stoichiometry of a reaction, write the various expressions for the rate of the reaction, and determine the relationship between them.

14 Given a table of concentration as a function of time for a reagent, determine an initial rate for the reaction.

15 Suggest (or select from supplied suggestions) possible rate expressions for simple reactions given their stoichiometry.

16 Given a (simple) rate expression and the rate data (as in Objective 14 say), determine the rate constant for a reaction.

Unit 12

17 Draw a sketch (or select a correct sketch) illustrating the way rate constants vary with temperature.

18 Define (or recognize a correct definition of) activation energy.

19 Recognize the Arrhenius equation.

20 Define (or recognize correct definitions of) the equilibrium constant for simple homogeneous reactions.

21 Calculate the value of an equilibrium constant, given the values of the concentrations of the reactant species at equilibrium.

- 22 Given the value of the equilibrium constant, calculate the percentage of various reactants at equilibrium for simple reactions.
- 23 Relate in general terms (for example, Le Chatelier's Principle) how the equilibrium constant varies with temperature for (a) exothermic reactions, (b) endothermic reactions.
- 24 Draw a sketch (or recognize a correct sketch) showing how equilibrium constants vary with temperature.
- 25 Relate the way the rate constant and the equilibrium constant vary with temperature to a reaction co-ordinate plot.
- 26 Define the role of a catalyst.
- 27 Relate the role of a catalyst to a reaction co-ordinate.
- 28 List the requirements for a reaction to occur.

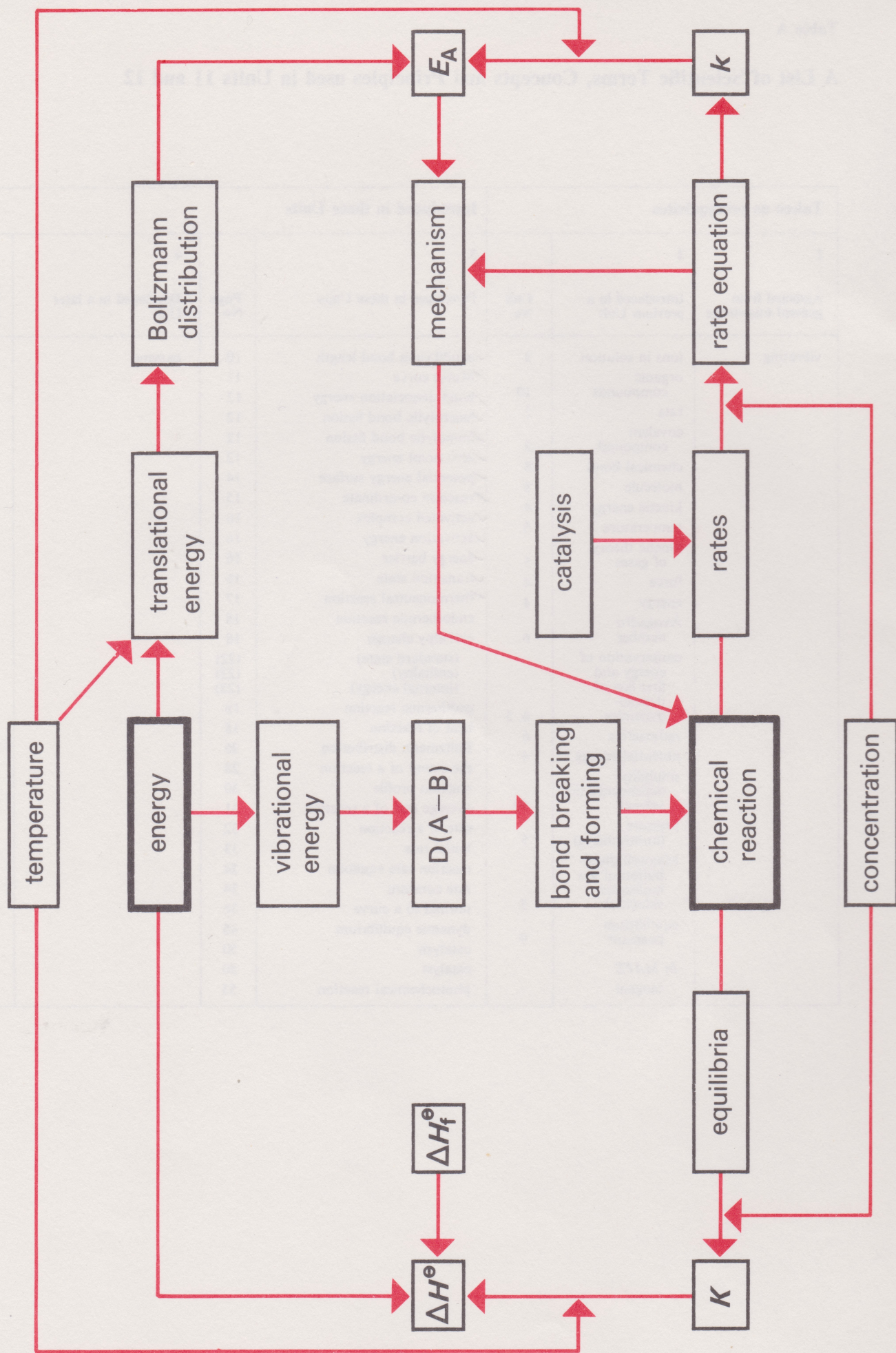
Home Experiments

- 29 Operate and understand the operation of the colorimeter in the Home Experiment Kit.
- 30 Determine the concentration of a reagent in a solution by using the colorimeter and a calibration graph which you have prepared.
- 31 Follow and determine the rate of a chemical reaction in which a coloured reagent is involved.
- 32 Determine an equilibrium constant for a reaction in which a coloured reagent is involved.

Table A

A List of Scientific Terms, Concepts and Principles used in Units 11 and 12

Taken as prerequisites			Introduced in these Units			
1	2		3		4	
Assumed from general knowledge	Introduced in a previous Unit	Unit No.	Developed in these Units	Page No.	Developed in a later Unit	Unit No.
vibrating	ions in solution	9	✓equilibrium bond length	10	enzyme	14
	organic compounds	10	✓Morse curve	11		
	rate	2	✓bond dissociation energy	12		
	covalent compound	8	✓heterolytic bond fission	12		
	chemical bond	8	✓homolytic bond fission	12		
	molecule	8	✓zero point energy	12		
	kinetic energy	4	✓potential energy surface	14		
	temperature	5	✓reaction co-ordinate	15		
	kinetic theory of gases	5	✓activated complex	16		
	force	4	✓activation energy	16		
	energy	4	✓energy barrier	16		
	Avogadro number	6	✓transition state	16		
	conservation of energy and first law of thermodynamics	4, 5	✓thermoneutral reaction	17		
	radioactive	6	endothermic reaction	18		
	potential energy	4	enthalpy change	18		
	solubility dependence on solvent	10	(standard state)	(22)		
	pressure (atmospheres)	5	(enthalpy)	(23)		
	Maxwell distribution of gas molecular velocities	5	(internal energy)	(23)		
	equilibrium constant	9	exothermic reaction	18		
	<i>In MAFS</i>		heat of reaction	18		
	tangent		Boltzmann distribution	26		
			the extent of a reaction	28		
			reaction profile	30		
			average rate of a reaction	31		
			rate of a reaction	32		
			initial rate	33		
			reaction rate equation	34		
			rate constant	34		
			normal to a curve	36		
			dynamic equilibrium	45		
			catalysis	50		
			catalyst	50		
			photochemical reaction	53		



Section 1

11.0 Introduction

In the last two Units you have studied some reactions of ions in solution (Unit 9) and of organic compounds (Unit 10). You have seen examples of what happens in specific chemical reactions and will have gained, in some of these cases, an idea of why reaction occurs and how it occurs. This Unit and the next will consider these questions in more detail.

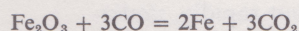
Before you read any further, make a list of the first questions you would ask about any particular chemical reaction and compare it with the list below.

The questions of practical interest are:

- (i) Under what conditions, if any, will the reaction occur?
- (ii) What is the yield of the reaction (or what are the equilibrium concentrations)?
- (iii) How fast will the reaction go?
- (iv) Can either the yield or the rate of the reaction be improved?

There is one obvious way of answering these questions—try it and see. Even today this is probably the most frequently used method, but it can be both costly and time consuming and never gives a complete answer to questions (i) or (iv), because there could always be some other sets of conditions that have not been thought of. The following quotation illustrates the problem of the practical approach.

It is known that in the blast furnace the reduction of iron oxide is produced by carbon monoxide, according to the reaction



but the gas leaving the chimney contains a considerable proportion of carbon monoxide, which thus carries away an important quantity of unutilized heat. Because this incomplete reaction was thought to be due to an insufficiently prolonged contact between carbon monoxide and the iron ore, the dimensions of the furnaces have been increased. In England they have been made as high as thirty metres. But the proportion of carbon monoxide escaping has not diminished, thus demonstrating, by an experiment costing several hundred thousand francs, that the reduction of iron oxide by carbon monoxide is a limited reaction. Acquaintance with the laws of chemical equilibrium would have permitted the same conclusion to be reached more rapidly and far more economically.

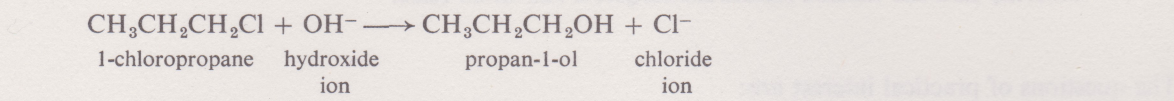
(Reference: H. Le Chatelier, *Ann. mines*, (8) **13**, 157 (1888).)

From what you learnt in Unit 10 you will probably expect that, before dealing with the above questions, one must first answer another one:

- (v) How does the reaction occur at the molecular level?

You will perhaps be surprised to learn that the answer to question (ii) *does not require* an answer to question (v). The actual rates and equilibria (yields) of reactions are of direct interest to a technologist. However, to a scientist, they are mainly of interest because he uses them to help him to predict and test models of the way the reactions are occurring at the molecular level.

In these two Units we shall reverse this procedure and start by assuming that we know how reactions occur at the molecular level, and by con-



One C—Cl bond is broken and one C—O bond is formed.

1

A diagram, based on this analogy, showing the energy required to produce various displacements about the equilibrium position would look like Figure 1.

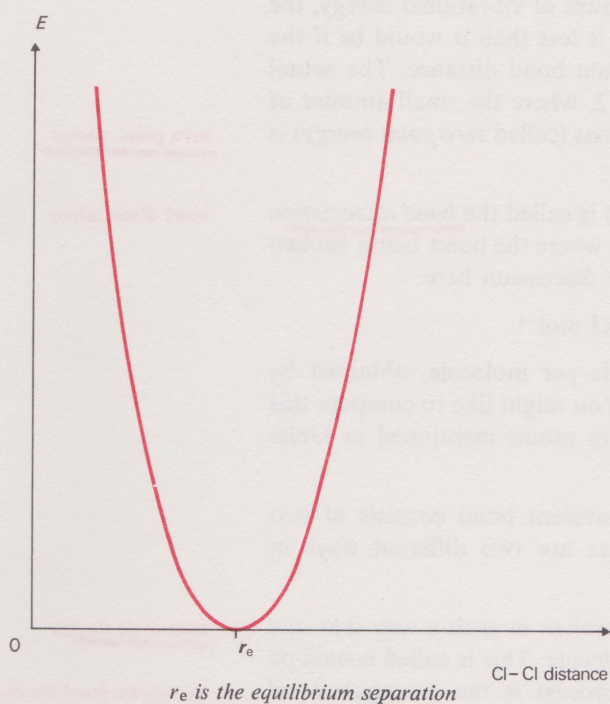


Figure 1 Energy versus separation for small displacements.

For small displacements from equilibrium, the spring model behaves in exactly the same way as a molecule. For larger displacements the behaviour of a molecule is shown more correctly in Figure 2.

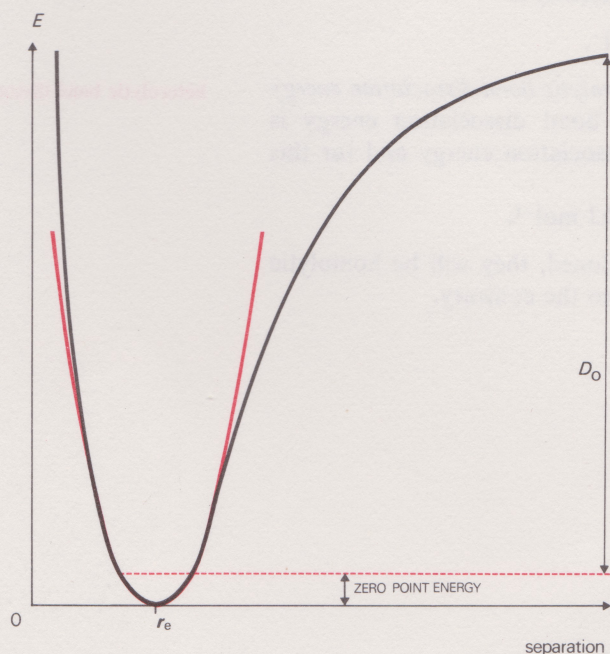


Figure 2 Morse curve.

This is called a Morse curve. It shows much the same rapid increase in energy required to push the two atoms closer together as the curve for small displacements (Fig. 1). But with increasing separation of the atoms,

Morse curve

the Morse curve flattens out. Obviously, it becomes easier to separate the atoms until finally no attractive force remains between them. At this point, of course, the bond (chlorine chlorine) is broken.

Because molecules *always* have a small amount of vibrational energy, the energy required to separate the two atoms is less than it would be if the atoms were initially at rest at the equilibrium bond distance. The actual energy required is shown as D_0 on Figure 2, where the small amount of vibrational energy that the molecule always has (called *zero point energy*) is also shown.

zero point energy

The energy required to break the bond (D_0) is called the bond dissociation energy and can be represented by $D(\text{Cl}-\text{Cl})$ where the bond being broken is indicated by the dash. In the case under discussion here

bond dissociation

$$D(\text{Cl}-\text{Cl}) = 243.36 \text{ kJ mol}^{-1}.$$

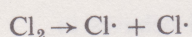
(This value is equivalent to 4×10^{-19} joule per molecule, obtained by dividing 243.36 by the Avogadro number. You might like to compare this with some of the electronic energy levels in atoms mentioned in Units 6 and 7.)

You will remember from Unit 8 that a covalent bond consists of two electrons shared between two atoms. There are two different ways in which such a bond can be broken.

(a) *Homolytic* fission*. The bond can be broken in such a way that one electron goes with each fragment of the molecule. This is called *homolytic fission* and the energy required for this process is the *homolytic bond dissociation energy* and is written (for chlorine) $D(\text{Cl}-\text{Cl})$ as above. For chlorine, it is the energy required for the reaction

homolytic fission

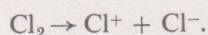
homolytic bond dissociation energy



(where the dot indicates an unpaired electron).

(b) *Heterolytic* fission*. The other way a bond can be broken is such that *both* electrons in the bond finish up with one fragment. The fragments are then ions and the reaction involved (for chlorine) is

heterolytic fission



The energy for the process is called the *heterolytic bond dissociation energy* and is written $D(\text{Cl}^+\text{Cl}^-)$. The heterolytic bond dissociation energy is much greater than the homolytic bond dissociation energy and for this case

heterolytic bond dissociation energy

$$D(\text{Cl}^+\text{Cl}^-) = 1137.8 \text{ kJ mol}^{-1}.$$

When bond dissociation energies are mentioned, they will be homolytic bond dissociation energies unless specified to the contrary.

* Derivation: homo = *same*; hetero = *different*; lysis, lytic = *splitting*.

11.1.2 An atom and diatomic molecule reaction

The reverse process to bond breaking, that is, bond formation, results in the release of energy.

How much energy would be released if two chlorine atoms formed a chlorine molecule?

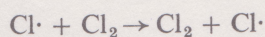
By the law of conservation of energy, the energy released must be the same as the energy required to break the bond, that is, $243.36 \text{ kJ mol}^{-1}$.

An interesting problem created by this energy is discussed in the black-page Appendix 2, p. 37.

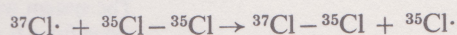
Having talked about bond breaking in the simplest type of case we shall now consider a reaction slightly more complex, that is, a reaction in which an atom reacts with a diatomic molecule to form a new diatomic molecule and another atom, *all reactants and products being gases*.



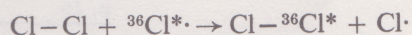
Even simpler from a theoretical point of view would be



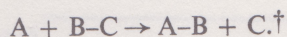
This may not look like a chemical reaction, because chemically the reactants and products are the same. However, bonds are broken and formed and if we used a different isotope of chlorine we could follow the progress of the reaction, for example



We could follow the reaction more easily if one of the atoms was an artificially prepared radioactive isotope, $^{36}\text{Cl}^*$ (the asterisk representing a radioactive nucleus) say,



For convenience in referring to the reaction, we shall consider it for a while as



Now picture the reaction on an atomic level. You can picture this as A approaching B-C, and work out the energy with A, B and C in various relative positions. The most favourable way for A to approach B-C turns out to be along the line B-C. This is rather convenient, because it is the approach for which the energy can be most easily calculated and also most conveniently represented graphically.

In this particular case (A approaching along the line B-C) the energy simply depends on the two distances, AB and BC,[†] so that we can represent the energy and these two distances with a three-dimensional model. Each possible value of the distances AB and BC will give the whole system a particular energy.

The two distances AB and BC will define the positions of the three atoms (remember that they are confined to one straight line).

We can show the possible positions of the atoms on a diagram using AB as one axis and BC as the other. Figure 3 is such a diagram (p. 14).

[†] For this hypothetical reaction, the notation A-B, B-C, etc. is used to represent a molecule in order to avoid confusion with the interatomic distances denoted by AB, BC, etc.

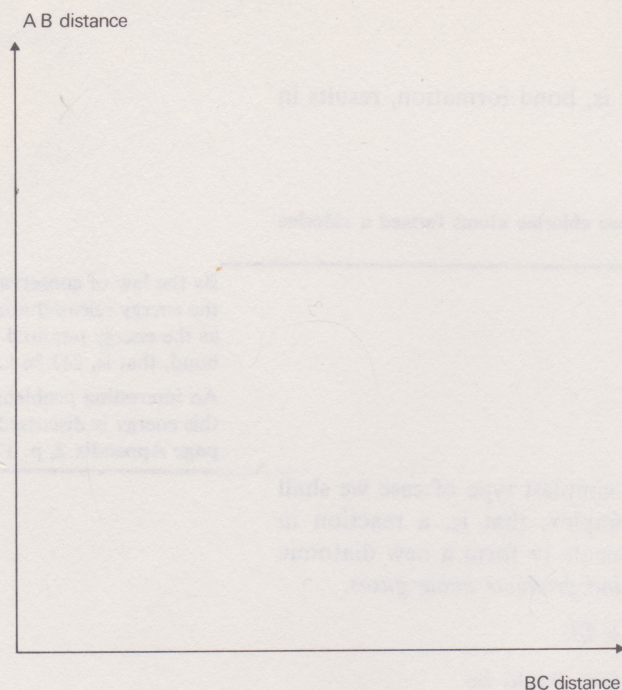


Figure 3 Geometry of the system A, B and C.

Mark a cross on the diagram to show the arrangement of the system before reaction takes place, when A is a long way from BC. That is, represent the system

A B-C

The system will then have a large value for AB and a small value for BC, the latter being the equilibrium bond length of B-C. So the cross should be near the AB axis near the top of the graph, as shown in Figure 4, p. 16.

Now put a similar cross on Figure 3, to show the arrangement when the reaction is over, and encircle roughly the area that represents the arrangement when reaction is actually taking place.

After reaction we have molecule A-B and atom C, so the BC distance is large and the AB distance is the A-B bond length.

The second cross is near the BC axis far from the AB axis. When reaction is taking place, all three atoms will be close together. Both crosses and the reaction area are shown on Figure 5. (p. 16).

The energy of the system can be represented as a third dimension on the graph and will result in a point above the distance plane (the plane of the paper) for every value of AB and BC, that is, for every arrangement of the three atoms. The points make a surface when joined. The height of the surface at any particular point represents the energy of the system at that particular value of AB and BC. Figure 6 is a photograph of such a surface.

11.1.3 The potential energy surface

The most obvious feature of this surface—called a *potential energy surface*—is that it contains deep *valleys* that are energy minima.

In general, systems tend to be in arrangements of minimum energy (common experience has probably suggested this to you many times—‘water runs downhill’ being a typical example). So the floors of the valleys on the potential energy surface will represent the arrangements of the three atoms that are most stable.

Before reaction takes place, when A is far from B-C, the potential energy of the system depends only on the BC distance, and the shape of the valley

potential energy surface

(cross-section at given AB distance with AB large) is given by the B-C Morse curve. (Marked on Figure 6.) Similarly, the energy of the products of the reaction (when C is far from A-B) is determined by the AB separation, and the valley has the shape (cross-section at constant large BC distance) of the A-B Morse curve. Because the system will endeavour to keep, as far as possible, to a minimum energy, the course of the reaction will be represented by a journey along the valley from reactants to products. This valley has a col at its highest energy point, a path over this col being the lowest energy path from the valley representing reactants to that representing products.

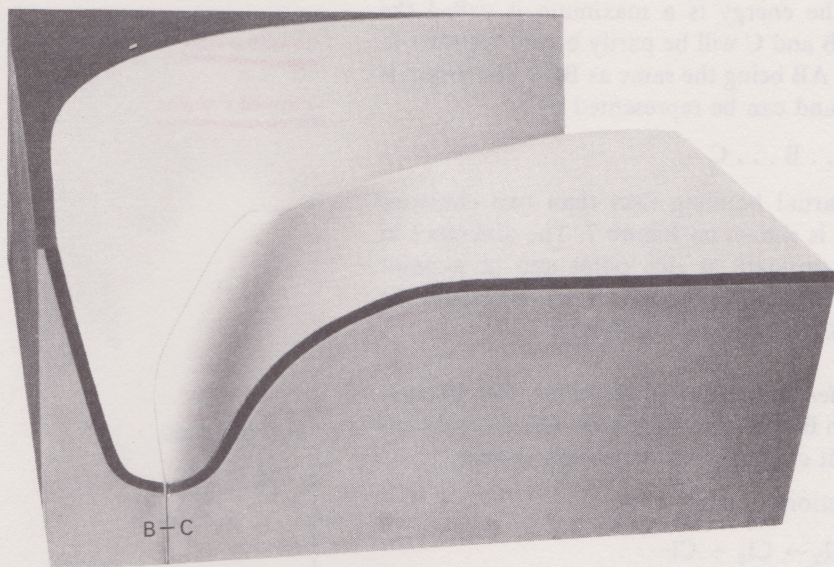


Figure 6 Potential energy surface.

A line along the floor of the valley and going over the col is the lowest energy path from reactants to products and is called the *reaction co-ordinate*. The distance along the reaction co-ordinate can be plotted against energy. Figure 7 shows the plot from the model in Figure 6.

reaction co-ordinate

What is happening along this path?

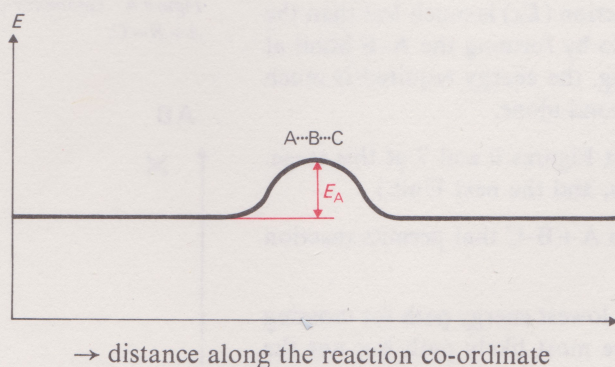


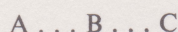
Figure 7 Reaction co-ordinate.

The effect of the reaction is that an electron originally localized between B and C ends up localized between A and B. When A gets quite close to B-C it will enter a region where repulsive forces are strong enough to oppose any closer approach unless the system has enough energy to overcome these forces.

Can you think of any forces of repulsion that might be present?

At the same time, the electrons around B–C will start to be attracted by the nucleus A, so there will be effectively less electrons between B and C and so the bond B–C will be weaker and will lengthen (B, C nuclear repulsion.) This effect will continue until the system passes through an energy maximum beyond which the bonding between A and B increases and between B and C decreases to the extent that the situation is better described as an A–B molecule influenced by C, rather than a B–C molecule influenced by A.

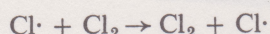
The state of the system when the energy is a maximum is called the *transition state*; all the atoms A, B and C will be partly bound together in a group (in our case, the distance AB being the same as BC). The group is also called an *activated complex* and can be represented by



where the dotted line implies partial bonding (less than two electrons shared between two atoms). This is shown on Figure 7. The difference in energy between the reaction co-ordinate at this point and at a point representing the energy of the reactants (A and B–C) is called *the activation energy* represented by E_A , also shown on Figure 7.

The col represents an *energy barrier* that has to be overcome. For reaction to take place, A has to collide with B–C so that the system (A, B and C) has more energy than E_A , otherwise it cannot cross the energy barrier.

The activation energy for the reaction



is

$$E_A \approx 20 \text{ kJ mol}^{-1}.$$

Compare this with the (homolytic) bond dissociation energy

$$D(\text{Cl} - \text{Cl}) = 243.36 \text{ kJ mol}^{-1}.$$

What do you deduce from this?

Perhaps the most important point to notice about these values (and the figures) is that the minimum energy for reaction (E_A) is much *less* than the energy required to break the bond B–C. So by forming the A–B bond at the same time as the B–C bond is breaking, the energy required is much less than that required to break the B–C bond alone.

There are a few more points to note about Figures 6 and 7 at this stage. (We shall return to these frequently in this, and the next Unit.)

- 1 E_A is the *minimum* energy of the system A + B–C that permits reaction to occur.
- 2 The reaction co-ordinate represents the lowest energy path for crossing from reactants to products, so it is the most likely path but not the only path.
- 3 The whole of Figure 6 (and hence Figure 7) applies to the reaction only when A approaches B–C along the line BC. In other words, the figures show reaction only for the case where A, B and C are always on one straight line.
- 4 Even for this restricted case you can see that the system (A, B and C) could get from reactants (A + B–C) to products (A–B + C) in many different ways. One would be by leaving the B–C valley in the fore-

There will be Coulomb forces of repulsion between the electrons on A and those on B and between the nuclei A and B.

transition state

activated complex

energy barrier

AB distance

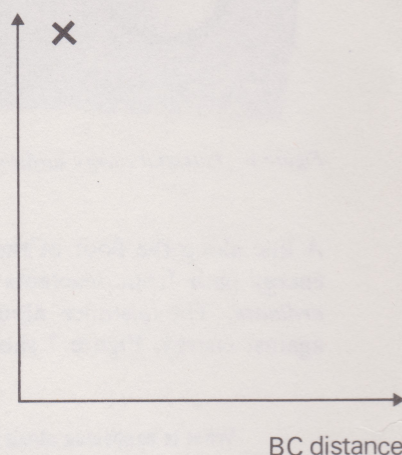


Figure 4 Geometry of the system A + B–C.

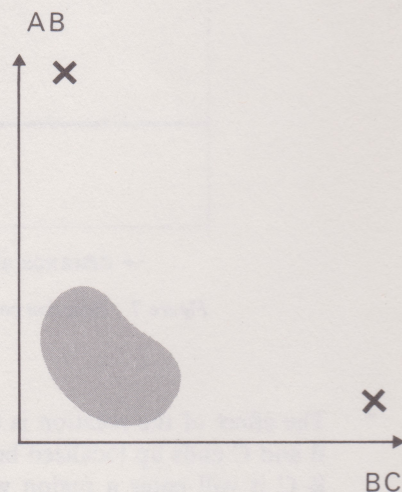


Figure 5 Geometry of the system A, B and C.

ground of Figure 6, crossing the plateau and dropping down into the A-B valley on the far right of Figure 6.

What would such a reaction path represent in terms of the atoms? Why is such a path unlikely?

We shall return later to the important question of where the system might obtain the energy needed for reaction. Assume for the time being that this energy is available, and concentrate now on the overall energy change in the reaction.

This would represent a situation where first the B-C bond was broken and then the A-B bond was formed. You can see from the figure that this requires much more energy to be put into the system and so is less likely.

11.1.4 The heat of reaction

In the simple reaction that we have been considering one bond is broken (B-C) and another is formed (A-B). The formation of A-B will result in release of energy. If the reaction follows the reaction co-ordinate, the energy released when A-B is formed will be much less than the bond dissociation energy $D(A-B)$, as you can see from Figure 6. Only if the bond was formed from completely separated A and B atoms would the energy released be $D(A-B)$. (This is the case discussed after point 4 above.)

In the case we set out to consider,



because the bond formed is the same as that broken, the overall energy change in the reaction *must* be zero.

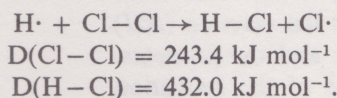
Does this mean that there is no energy barrier to the reaction?

No. The reaction still needs E_A available; but this energy is then returned to the system.

Reactions like this, where there is no overall energy change for the reaction, are called *thermoneutral*.

thermoneutral reaction

What if the bond being formed has a larger bond dissociation energy than the bond being broken? For example, for the reaction



What is the overall energy change for the reaction?

The answer to that question incorporates a very important idea. The calculation assumes that the *overall* energy change for the reaction does not depend on the path the reaction takes. The path actually used in the calculation is the one discussed after point 4 earlier. This, as you have seen from the potential energy surface, is an unlikely path but is useful for calculation purposes.

As $D(\text{H}-\text{Cl})$ is greater than $D(\text{Cl}-\text{Cl})$ more energy is released than used.
 $D(\text{H}-\text{Cl}) - D(\text{Cl}-\text{Cl}) =$
 $188.6 \text{ kJ mol}^{-1}$
is the overall energy change for the reaction and this energy is released.

The fact that the overall energy change does not depend on the path is an application of the Law of Conservation of Energy or the First Law of Thermodynamics (cf. Unit 5).

If the overall energy change *did* depend on how the reaction was performed, a reaction could be performed along one path and then reversed along another path, finishing with the original reactants and having produced surplus energy; that is, a chemical perpetual motion machine, breaking the first law of thermodynamics, which is contrary to all past experience.

If the reaction is carried out at constant pressure, the actual energy change observed is called an *enthalpy change* (we shall return to this in section 11.2.3), and the enthalpy change of the reaction is called the *heat of reaction* and is denoted by the symbol ΔH .

So for the last reaction $\Delta H = -188.6 \text{ kJ mol}^{-1}$.

Note that ΔH is negative if heat is given out by the reaction, that is if the system (hydrogen atom and chlorine molecule) loses energy. This type of reaction (when energy is given out) is said to be *exothermic*.

enthalpy change

heat of reaction

exothermic reaction

How would you expect the heat of the reaction (the energy released) to show itself in this case?

The reaction co-ordinate for a reaction like this (where the system loses energy) would look like Figure 8.

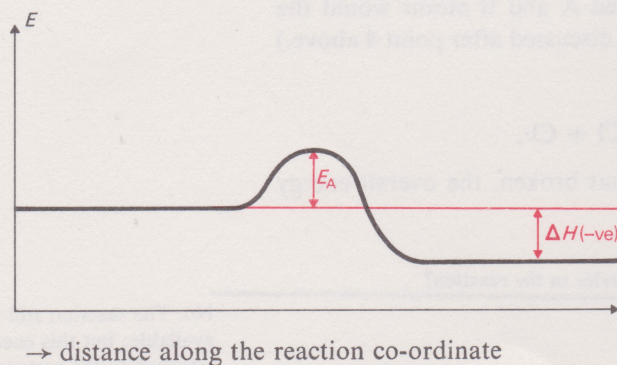
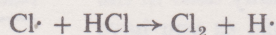


Figure 8 Reaction co-ordinate (exothermic reaction).

Note that in contrast to Figure 7, the products are now at a lower energy than the reactants. Notice that the activation energy is measured from the energy of the reactants. The enthalpy change for the reaction (ΔH) is the difference between the energy of the reactants and the products. Again notice that ΔH does not depend on the size of the activation energy, that is, on the path the reaction takes.

The alternative type of reaction is also possible, namely a reaction where the bonds formed have a lower bond dissociation energy than those broken. The overall energy change for the reaction results in energy being required by the reacting system. The first equation to hand is the reverse of the last reaction, i.e.



What is the value of ΔH for this reaction?

The reaction co-ordinate for this reaction is as shown in Figure 9. Reactions like this, that absorb energy (i.e. have ΔH positive) are called *endothermic*.

Clearly, $\Delta H = D(\text{Cl}-\text{Cl}) - D(\text{H}-\text{Cl})$
 $= +188.6 \text{ kJ mol}^{-1}$.

This is also required by the law of conservation of energy.

endothermic reaction

Figure 9 is, of course, just Figure 8 drawn backwards, but note that the activation energy for this reaction is not the same as before but is in fact bigger by ΔH .

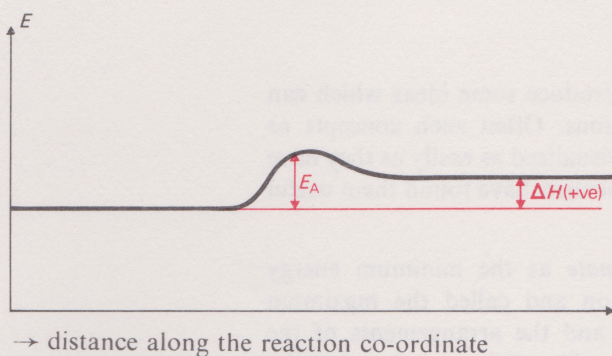


Figure 9 Reaction co-ordinate (endothermic reaction).

What have we established so far?

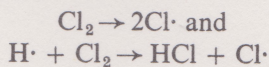
Dealing only with a diatomic molecule, we have defined the *bond dissociation energy*. Then, using a three atom system, we have introduced the *reaction co-ordinate*, *activation energy*, *transition state*, *activated complex* and the *heat of reaction* which is called the *enthalpy change* when the reaction is performed at constant pressure. We have introduced the idea of an *energy barrier* needing to be overcome during a reaction and shown that the heat of reaction (reaction enthalpy change) does not depend upon the reaction path.

Write down what you understand these terms to mean and draw reaction co-ordinates showing:

- (a) thermoneutral
- (b) exothermic
- (c) endothermic

reactions. Then turn back and compare what you have written and drawn with the text.

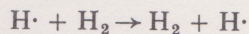
We have established these ideas for the simple reactions



How applicable are these ideas to other (more complex) reactions?

It is possible to draw Morse curves for most diatomic molecules. These correctly give the bond dissociation energy and other properties. However, only approximate curves can be obtained for more complex cases, for example, for $\text{D}(\text{CH}_3-\text{H})$ which is the bond dissociation energy for a C-H bond in methane. These bond dissociation energies can however often be measured directly or calculated semi-empirically.

Although it is possible to compute a potential energy surface for the reaction



the best calculations made so far still do not result in accurate activation energies. But even the reaction we dealt with above requires approximations; usually the activation energy is determined experimentally (see later) and used to help construct the surface.

In spite of the above, the ideas that have been introduced in this Unit are generally helpful in understanding the role that energy plays in chemical reactions.

11.1.5 Summary

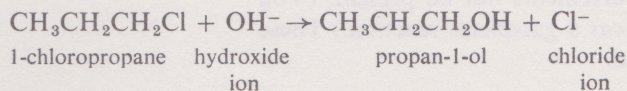
We have used these simple reactions to introduce some ideas which can be applied to much more complex reactions. Often such concepts as reaction co-ordinate will not be able to be visualized as easily as they have been in this simple case, but nevertheless chemists have found them useful for thinking about all reactions.

We have introduced the *reaction co-ordinate* as the minimum energy (hence, most favourable) path for reaction and called the maximum energy point on this the *transition state*, and the arrangements of the atoms at that point an *activated complex*. The difference between the energy at this point and the energy of the reactants is called the *activation energy* and represents an *energy barrier* that has to be overcome for the reaction to take place. We have also used the reaction co-ordinate to illustrate the overall energy change, called the *enthalpy change*, for a reaction. If you are not sure of the meaning of any of the terms in italics you should go back over section 11.1.

11.2.1 A substitution reaction

We shall now apply some of these ideas to specific reactions to see their uses and limitations.

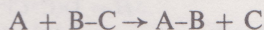
Consider the substitution reaction below, which is an example of the type discussed in Unit 10 (section 10.5.5).



How many dimensions would be needed to plot the potential energy surface for this reaction?

There are 13 atoms involved in this reaction. This means that 33 position co-ordinates are required just to fix the relative *positions* of the atoms. (Each atom would require 3 position co-ordinates; a value for *x*, *y* and *z* in a Cartesian frame of reference. However, this would *fix* the molecules in space and we only want the relative positions of the atoms, so six less co-ordinates are required. Do not worry if you cannot follow this in detail. The idea that a large number of co-ordinates is needed is obvious enough.) As well as fixing the relative positions of all the atoms, we need another dimension to give the energy of the system.

Clearly this is rather a daunting task. However, the situation can be greatly simplified. For example, the approach of the OH^- might be restricted to a supposed (guessed) most favourable direction and the system treated as a pseudo three-atom problem where for



A is taken as OH^-

B is taken as $\text{CH}_3\text{CH}_2\text{CH}_2^+$ and

C as Cl^- .

The same type of reaction co-ordinate as in section 11.1.4 could then be used to represent the path of the reaction. The basis for this procedure is sound enough. That is, there *will* be:

- (a) a lowest energy path for reaction,
- (b) an energy barrier, and hence
- (c) an activation energy, and
- (d) an activated complex—that is, the arrangement of the (13) atoms at the maximum energy along the most favourable reaction path (that is, at the transition state).

However, the reaction co-ordinate used will be a gross simplification. Even if the direction of approach of the OH^- were to be along some pre-determined path it will not only influence the C–Cl bond as it approaches but to a smaller or greater extent have an influence on *all* the other bonds in the activated complex.

This means that, while the ideas are useful and while the diagram of the reaction co-ordinate could show the correct activation energy (E_A) and the correct heat of reaction (enthalpy change ΔH), both determined experimentally, the other features (shape of the energy barrier for example) would merely be general representations of the ideas.

An important factor in this reaction has been completely ignored in the above treatment. Can you see what this is?

The reaction was carried out in solution, that is, in intimate contact with solvent molecules.

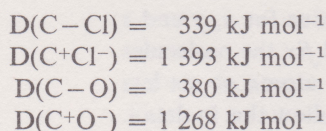
In Unit 10 we pointed out that the solubility of a compound depends on the nature of the solvent, and that polar solvent molecules group themselves around polar solutes, and they do so even more strongly around ions.

Clearly a correct potential energy surface for the reaction should include at least some of the solvent molecules, and so should the activated complex. Only in reactions of gases will such involvements not be present. (You will remember that our simple example was a gas-phase reaction.) These limitations should always be kept in mind.

11.2.2 Enthalpy change

Think about this reaction in a bit more detail.

Here are some relevant bond dissociation energies.



What is the enthalpy change in this reaction? Is the reaction endothermic or exothermic?

When we quote a value for ΔH for this reaction in kJ mol^{-1} , we are clearly referring to a certain amount of reaction (1 mole). 125 kJ is the enthalpy change for the conversion of 1 mole (78.5 g) of 1-chloropropane into 1 mole (60 g) of propan-1-ol, the reaction being carried out at constant pressure. If you had missed this last point, look back to the first mention of enthalpy in section 11.1.4. When you mix two reagents in beakers you are performing the reaction at constant (atmospheric) pressure.

The reaction involves ions, so the heterolytic bond dissociation energies are relevant. The heat of reaction would be

$$\begin{aligned}\Delta H &= D(\text{C}^+\text{Cl}^-) - D(\text{C}^+\text{O}^-) \\&= 1\,393 - 1\,268 \\&= +125 \text{ kJ mol}^{-1}.\end{aligned}$$

The reaction is endothermic, that is, heat is needed for the reaction. (These numbers, in fact, should only be used for gas reactions at 298 K but we use them here as a first approximation.)

What is the enthalpy change if 7.85 g of 1-chloropropane were converted to 6.0 g of propan-1-ol?

We are converting $\frac{1}{10}$ of a mole and hence breaking and forming $\frac{1}{10}$ the number of bonds, so the enthalpy change would be 12.5 kJ.

Do any other factors except the amount of material reacting affect the enthalpy change? Yes, the enthalpy change can vary with temperature and even (because of the interaction of the solvent) with concentration and pressure. So when ΔH values are specified they do not mean anything unless the conditions they refer to are known. To avoid having to state conditions every time a ΔH is quoted, a convention is adopted of using one certain set of conditions called a *standard state*. The values for these conditions are then shown as $\Delta H^\ominus$, where the superscript $\ominus$ shows that standard states are being referred to.

standard state

11.2.3 Standard enthalpy changes

By convention the standard state is the pure substance in its stable state (gas, liquid or solid) at one atmosphere pressure, and at a specified temperature. Most frequently, values are quoted for 298 K (see Unit 5) which is 15° C and this is sometimes implied in the standard state. There are also standard states for solutions which need not concern us here.

In the above case, if the reactants and products were in their standard states (one atmosphere pressure and the standard state for solutions) then we would write

$$\Delta H^\circ(348 \text{ K}) = 125 \text{ kJ mol}^{-1}$$

where the number in brackets is the temperature (in kelvin) for which this is the standard heat of reaction.

Previously, in this Course, we have used Δ to indicate either a part of something or a change in something. Here we use it in the latter sense. ΔH is the change in enthalpy of the system when reactants turn into products. This implies that we must be able to write

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

where $H(\text{products})$ is the enthalpy of the products.

What is enthalpy?

Enthalpy is a convenient thermodynamic function which depends on the state of a system, that is, only its temperature, pressure, composition, etc. *not* on how it got to this temperature, etc.

You have already seen one illustration of its convenience; the change in enthalpy in a chemical reaction is the heat of the reaction.

Enthalpy is defined as the value of the *internal energy* (U) of the system to which is added the product of its pressure and volume.

internal energy

$$H = U + pV$$

Pressure and volume you are familiar with, but internal energy is a new concept. In total the internal energy of a system consists of the kinetic energy of its molecules and the potential energy due to their interaction, together with any vibrational and rotational energy of the system. To this should be added any nuclear energy and electronic energy of the various atoms in the system, and in fact there is no end to the types of energy that go to make up the internal energy of the system.

In fact, we cannot measure the internal energy of a system and hence we cannot determine H . WE CAN MEASURE ONLY CHANGES IN INTERNAL ENERGY AND ENTHALPY.

This has not prevented enthalpy from being a very useful function of a system. The problem of enthalpy not having an absolute value is overcome by defining an *enthalpy of formation* of a substance. The enthalpy of formation of a substance is defined as the enthalpy change in the reaction which forms the substance *from its elements*, all substances being present in their standard states. Enthalpies of formation are written

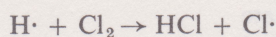
enthalpy of formation

$$\Delta H_f^\circ$$

where the f stands for 'formation' and the $^\circ$ indicates standard states as usual.

For most purposes, enthalpies of formation can be treated as if they were actual enthalpies of substances.

To show how the values of $\Delta H_f^\ominus$ can be used, consider the reaction treated above



For this reaction

$$\Delta H_f^\ominus (\text{H}\cdot) = 218 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus (\text{Cl}_2) = 0 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus (\text{HCl}) = -92 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus (\text{Cl}\cdot) = 122 \text{ kJ mol}^{-1}.$$

So that $\Delta H^\ominus$ for the reaction is given by

$$\begin{aligned} \Delta H^\ominus &= H^\ominus(\text{products}) - H^\ominus(\text{reactants}) \\ &= -92 + 122 - (0 + 218) \\ &= -188 \text{ kJ mol}^{-1}. \end{aligned}$$

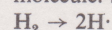
Note that the standard state referred to is 1 atmosphere pressure and all the above figures are quoted for 298 K. The value of 0 for chlorine may look odd to you. This is because of the way the enthalpy of formation of a substance is defined.

Cl_2 gas at 1 atmosphere is the standard state of chlorine so by definition its enthalpy of formation must be zero.

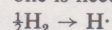
The other thing that might surprise you about the above enthalpies of formation is that $\Delta H_f^\ominus$ for HCl is negative whereas $\Delta H_f^\ominus$ for the atoms is positive.

Write down the reaction that $\Delta H_f^\ominus (\text{H}\cdot)$ refers to. Look back at the definition of standard enthalpies of formation as a guide.

For $\Delta H_f^\ominus (\text{H}\cdot)$ the reaction is the one that forms $\text{H}\cdot$ from the standard state for hydrogen which is the molecule. So



But this forms two H-atoms, and only one is needed, so the reaction is

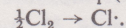


$\Delta H^\ominus$ for this reaction is

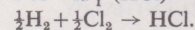
$$\Delta H_f^\ominus (\text{H}\cdot) = 218 \text{ kJ mol}^{-1}.$$

Now write the reactions for $\Delta H_f^\ominus (\text{Cl}\cdot)$ and $\Delta H_f^\ominus (\text{HCl})$.

For $\Delta H_f^\ominus (\text{Cl}\cdot)$



For $\Delta H_f^\ominus (\text{HCl})$



If you concentrate on the reactions that the standard enthalpies of formation refer to, you should see why $\Delta H_f^\ominus$ for atoms is positive. In these reactions bonds are being broken but not formed so energy will be required and hence $\Delta H_f^\ominus$ is positive. Clearly, the result for HCl ($\Delta H_f^\ominus (\text{HCl})$) depends on the relative bond dissociation energies of H_2 , Cl_2 and HCl.

The negative value, indicating that heat is given out in the reaction, means that the products (HCl) are at a lower energy than the reactants. If we assume that lower energy arrangements are more stable (as we did in section 11.2 when dealing with the potential energy surface) then HCl is stable *with respect to* H_2 and Cl_2 . This last qualification is important because the value of ΔH (and its sign) found above applies *only* to the particular reaction we are considering.

ΔH_f° for $H\cdot$ is given above. What is the bond dissociation energy for hydrogen?

ΔH_f° is 218.0 kJ mol⁻¹ and this, as shown above, is ΔH° for the reaction $\frac{1}{2}H_2 \rightarrow H\cdot$

The bond dissociation energy is the ΔH° for the reaction $H_2 \rightarrow 2H\cdot$

So $D(H-H) = 2 \times \Delta H_f^\circ(H\cdot)$
 $= 436 \text{ kJ mol}^{-1}$

11.2.4 Summary

So far, we have discussed the two ways energy considerations affect chemical reactions. They are:

- 1 There is a minimum energy for reaction, the activation energy, which (in the cases discussed so far) must be positive.
- 2 The overall energy change in a reaction, that is, the value of ΔH . This can be:
 - (a) positive (endothermic reaction) when energy is taken from the surroundings,
 - (b) zero (thermoneutral reaction),
 - (c) negative (exothermic reaction) when energy is given to the surroundings.

Whatever the value of the overall energy change there is still an activation energy.

Section 3

11.3.1 The energy required for reaction to occur

This is a suitable point to return to the question mentioned in section 11.2.3 of how the energy for reaction can be obtained.

Again, this is most easily discussed in terms of our simplified reaction



Figure 6 shows the potential energy surface of the system, and reaction can occur if the system has sufficient energy to pass over the energy barrier. Where can the system obtain this energy? You probably realize that this energy is the energy of the collision (of A with B-C) and the energy of the system is just the relative kinetic energy of the two reactants. That is, if you could sit at the collision point, it is the total kinetic energy of approach of A and B-C.

Another source of energy is relevant and this has been discussed in section 11.1.1.

What is this other source of energy?

The energy of the system, as far as reaction is concerned, is the relative kinetic energy of the reactant molecules and any relevant vibrational energy. If all the molecules in a gas had the same kinetic energy, then, when this energy was equal to or greater than the activation energy, reaction could take place every time there was a collision between an A and a B-C. If the kinetic energy and vibrational energy is less than the activation energy then no reaction could occur.

The molecule B-C always has some vibrational energy and, in our case, this will be along the line of the three atoms. In the Morse curve you saw that the energy of B-C was always higher than it would be if the molecule were actually stationary at its equilibrium separation.

11.3.2 The Boltzmann distribution

As you know from Unit 5, although it is possible to talk about the average kinetic energy of molecules in a gas (this energy is related to the temperature of the gas), at any time there is a large range of velocities (and hence, kinetic energies) of the molecules in a gas. The actual distribution of energies for simple systems is given by the *Boltzmann distribution*. This is illustrated graphically in Figure 10.

Boltzmann distribution

This graph should look familiar to you. It is very similar to the Maxwell distribution of velocities you saw in Unit 5.

Figure 10 applies only to a given temperature. If the temperature is increased what is the effect on the molecules and how will the curve alter?

Obviously, the average kinetic energy has to increase, so you would expect the peak in the curve to move to the right. The other thing that happens is that the *spread* of energies also increases. Two curves at different temperatures are shown in Figure 11.

The red curve is for a higher temperature. You will note that the peak in the curve has indeed shifted to the right, giving a higher average kinetic energy. The other thing that will no doubt strike you is that the peak is lower.

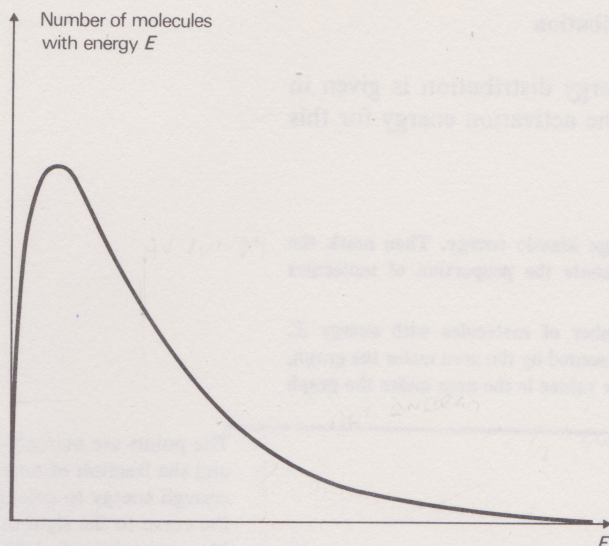


Figure 10 The Boltzmann distribution.

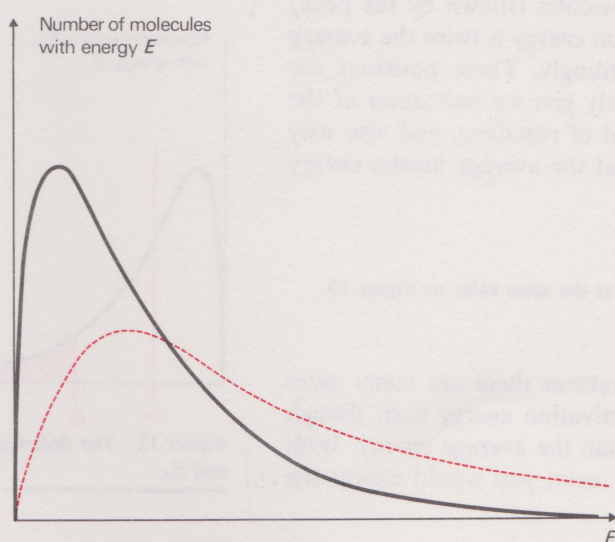


Figure 11 Boltzmann distribution $T_2 > T_1$.

Can you think of the reason for this? It is implied in the last but one paragraph on p. 26.

A wider spread of energies implies fewer molecules with the average energy.

Because there are the same total number of molecules represented by each curve and the spread of energies is wider at a higher temperature there will be fewer molecules with the average energy as the temperature rises.

Can you now see the relevance of Figure 10 to the problem of the source of energy for reaction?

Read the first sentence of section 11.3.2 to remind yourself of the question. Then read the last two sentences in section 11.3.1 and look at Figure 10.

11.3.3 The activation energy and the Boltzmann distribution

Let us assume that the molecules whose energy distribution is given in Figure 10 can undergo a reaction and that the activation energy for this reaction is twice the average kinetic energy.

Mark on Figure 10 the approximate average kinetic energy. Then mark the activation energy for the reaction and estimate the proportion of molecules that have sufficient energy to react.

(Because Figure 10 is a graph of the number of molecules with energy E , the total number of molecules present is represented by the area under the graph, and the number with energy between any two values is the area under the graph between the two values of E .)

The curve in Figure 10 is not symmetrical. There are more molecules to the right of the maximum than to the left, so the average energy will not be the energy of the greatest number of molecules (shown by the peak) but will be a bit larger than this. The activation energy is twice the average kinetic energy and should be placed accordingly. These positions are shown on Figure 12. These ideas immediately give an indication of the effect of increasing temperature on the speed of reactions, and also why reactions can occur at temperatures such that the average kinetic energy of the molecules is less than E_A .

Mark Figure 11 with the activation energy at the same value as Figure 10.

Figure 11 shows you that at higher temperatures there are many more molecules with energies greater than the activation energy even though the activation energy is still much greater than the average energy. With more molecules having sufficient energy to react, you would expect the reaction to be much faster.

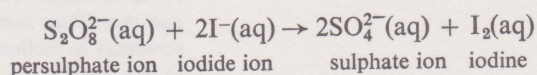
In general reactions double in rate (see next section) for every 10° rise in temperature.

We suggest that you should have attempted the Home Experiment for this Unit after reading section 11.4.1 and before studying sections 11.4.2 onwards. Later in this Unit we shall be referring to the graphs you should obtain in your experiment. If, however, for some reason you are unable to do the experiment by this stage, or if you are unable to obtain satisfactory results, we shall supply sample graphs, though we think it better for you to use your own.

11.4.1 The extent of a reaction

The last section talked about the effect of temperature on the speed of a reaction. Now we shall start being a little more specific about what we mean by the extent of a reaction and the speed or rate of a reaction.

Consider the Home Experiment reaction: the reaction of persulphate ion with iodide ion in aqueous solution.



The extent of the reaction at a given time could be measured by determining the amount of persulphate ion that had disappeared (been con-

The points are marked on Figure 12, and the fraction of molecules with enough energy to react (area under the curve to the right of E_A) looks like approximately $1/20$. How these answers were obtained is indicated in the following text.

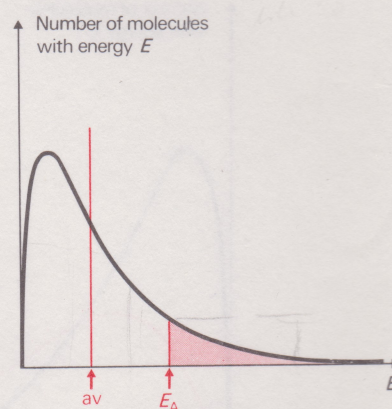


Figure 12 The Boltzmann distribution and E_A .

sumed). Alternatively, the amount of iodide ion that had been consumed could be determined.

Are they the same?

Another way of looking at the extent of a reaction is to determine the amount of product formed, in this case either sulphate ion or iodine.

No. From the stoichiometry two iodide ions are consumed for every persulphate ion. So the number of moles of iodide consumed in a given time would be twice the number of moles of persulphate ions consumed.

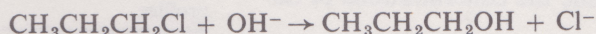
Take x as the amount, in moles, of persulphate consumed in a certain time.

- (a) How many moles of iodide ion will have been consumed?
- (b) How many moles of sulphate ion will be formed?
- (c) How many moles of iodine would be formed?

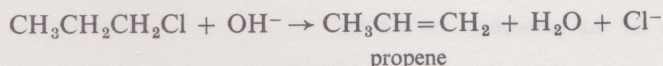
This question is immediately answered from the stoichiometry as indicated in the last question. The answers are:

- (a) $2x$,
- (b) $2x$,
- (c) x .

The relationship between the various concentrations concerned is, of course, given by the stoichiometry of the equation, *if* the stoichiometry represents the only reaction occurring. This is by no means always true. For example, the reagents in the reaction in section 11.2.1



can give different products:



and these two reactions compete.

Another possible complication is a subsequent reaction of the products. We shall not attempt to treat such complications in this course, though the possibility of their presence should always be kept in mind.

We have mentioned above the extent of reaction and you can probably visualize what is meant without much trouble, but if you want to be specific, how would you state the amount of reaction? You could give, in kilogrammes, the mass of reactant consumed. However, it is more informative to say how many molecules have been consumed. Because this number would be enormous for any amount of reaction you could normally detect, it is more convenient to use the number of moles of reactants consumed as a measure of the extent of reaction.

Later you will see that it is not so much the amount of material that influences the extent of reaction in a given time, but the concentration; so a more usual measure of the extent of reaction is the decrease in the concentration of reactant.

So,

extent of reaction = mole of reactant consumed
= mole of product formed,

or

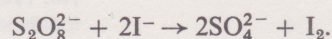
= decrease in concentration of reactant (mole per litre)
= concentration of product formed (mole per litre).

For this to indicate the extent of reaction you would also need to know the amount or concentration of reactant present at the start, so the best method is to give the percentage or fraction of reactant that has been consumed.

We suggest that you should attempt your Home Experiment at this stage if you have not already done so.

11.4.2 The reaction profile

From your Home Experiment (Experiment 1) you obtained a graph (Graph III) of the concentration of one of the products of the reaction against time for the reaction



We also performed the experiment but used a more concentrated solution of ammonium persulphate. Our results (colorimeter readings) are given in Table 1 (p. 31) and are plotted in Figure 13 (in concentrations).

This graph, showing the way a concentration varies with time, is a reaction profile. (It corresponds to your Graph III.)

reaction profile

Actually, Figure 13 is only part of a reaction profile, a complete reaction profile would show simultaneously the concentrations of all the molecules participating in the reaction, both reactants and products.

How would the reaction profile for the sulphate ion compare with Figure 13?

Because two sulphate ions are produced for every iodine molecule, the concentration of sulphate will always be twice that of iodine. Figure 14 is a sketch of the two profiles.

A complete reaction profile would also include the concentrations of the reactants.

On Figure 15 sketch the reaction profile for the persulphate ion for the experiment shown in Figure 13.

From Table 1 the initial concentration is 0.022 M. This is half the concentration of the prepared solution of persulphate because in the experiment the solution is diluted with an equal volume of iodide solution. Your sketch should start from 0.022 M and curve down mirroring Figure 13.

If you wanted to put specific points on Figure 15 (other than the point at $t = 0$) you should realize that every mole of persulphate ion consumed

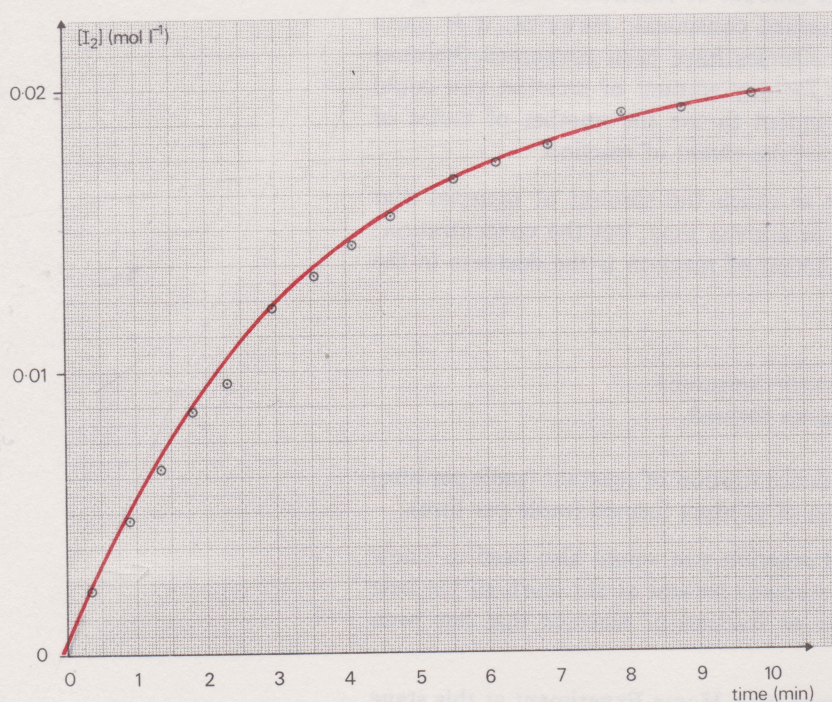


Figure 13 Experimental reaction profile (I_2).

produces one mole of iodine, so reading the concentrations of iodine at given times from Figure 13 enables you to calculate the concentration of persulphate left.

$$[S_2O_8^{2-}]_t = [S_2O_8^{2-}]_0 - [I_2]t$$

where the subscript indicates the time.* This relation is only true of course if the stoichiometry is correct and no other reactions are occurring. Figure 16 (p. 33) is a sketch of the persulphate ion concentration as a function of time for the experiment we performed (Table 1 and Fig. 13).

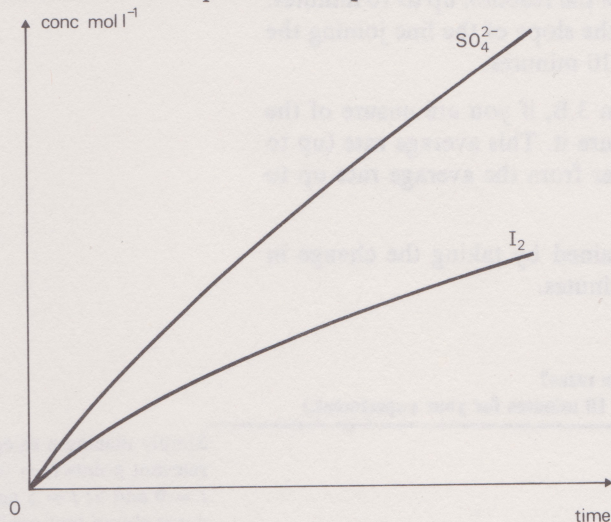


Figure 14 Reaction profiles for I_2 and SO_4^{2-} .

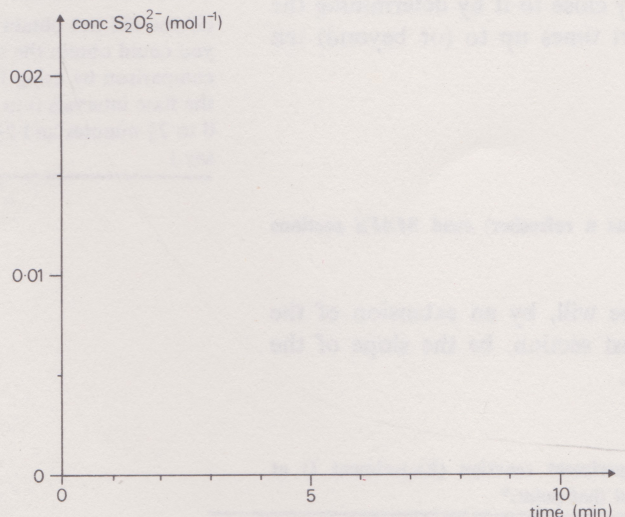


Figure 15 Reaction profile (student sketch).

11.4.3 Average rate of reaction

The third question posed in section 11.0 was ‘how fast will a reaction go?’ In the last section we talked about the extent of reaction in a given time so that we could easily calculate an average rate (or speed) of the reaction.

What was the average rate of your Home Experiment I for the first ten minutes?

Table 1 Colorimeter readings with time.
Concentrations of prepared solutions:
 $S_2O_8^{2-}$, 0.044 mol l⁻¹;
 I^- 0.30 mol l⁻¹.

Temperature: 20° C.

Time		Colorimeter reading
minutes	seconds	
0	00	100
0	22	90.5
0	53	82.0
1	20	72.0
1	48	63.5
2	14	59.5
3	00	48.0
3	32	43.0
4	06	38.5
4	40	34.5
5	35	29.0
6	10	26.0
6	53	23.5
7	55	18.5
8	50	18.0
9	46	16.2
—	—	—
65	00	6.25

The rate could be given as the concentration of I_2 produced, divided by the time. Our result at 5 minutes is on p. 32.

* This method of showing concentrations (square brackets) was introduced in Unit 9 (section 9.16).

For our experiments (Table 1) we have obtained the average rate up to 5 minutes. We read the concentration from the graph (Fig. 13—our Graph III) because we did not make a reading at exactly five minutes. This is an example of interpolation. Even if we had made a reading at five minutes it might have been better to read the value from the graph. The graph will smooth out some of the experimental errors and so may be more accurate than the individual points.

The result you obtained is the average rate of the reaction up to 10 minutes. It would be represented on your graph by the slope of the line joining the two points on the graph at $t = 0$ and $t = 10$ minutes.

Read *HED*, section 9.2 and *MAFS*, section 3.B, if you are unsure of the meaning of the term slope or how to measure it. This average rate (up to 10 minutes in your Experiment 1) will differ from the average rate up to 5 minutes—look at your Graph III.

Another average rate again could be obtained by taking the change in concentration of I_2 between five and ten minutes.

Which is the fastest of these three average rates?
(0 to 10 minutes, 0 to 5 minutes and 5 to 10 minutes for your experiment.)

None of these average rates really tells us how fast the reaction is going at ten minutes; though you could get very close to it by determining the increase in concentration of I_2 over short times up to (or beyond) ten minutes.

11.4.4 Rate of reaction

If you do not know any calculus (or as a refresher) read *MAFS* sections 5.A.1–5 before going further.

The actual rate of a reaction at any time will, by an extension of the procedure suggested at the end of the last section, be the slope of the *tangent* to the reaction profile at that time.

Calculate the rate of your Home Experiment reaction (Experiment I) at $t = 10$ minutes by drawing the tangent at that point.*

On Figure 13 we drew the tangent at $t = 5$ minutes and from it obtained the slope and hence the rate.

The rate, like the average rate, is measured as a concentration change in a particular time and so is in mole per litre per minute (say). It is more usual to give the rate as a concentration change per second so the rate per minute is divided by 60. We have, in effect, defined the rate of a reaction at a particular time. In calculus notation it is

$$\text{rate} = \frac{dc}{dt}$$

where c is the concentration of a product of the reaction.

* For two useful methods of drawing a tangent to a curve see Appendix 1, p. 36.

$$\begin{aligned}\text{Average rate} &= \frac{\text{concentration at 5 minutes}}{5 \text{ minutes}} \\ &= \frac{0.0158}{5} \\ &= 0.00316 \text{ mol l}^{-1} \text{ minute}^{-1}.\end{aligned}$$

$$\begin{aligned}\text{Average rate to 5 minutes} &= 3.16 \times 10^{-3} \text{ mol l}^{-1} \text{ minute}^{-1}.\end{aligned}$$

Simply placing a ruler joining the relevant points ($t = 0$ and 10; $t = 0$ and 5; $t = 5$ and 10) on the curve shows you qualitatively that the average rate for the first five minutes is the fastest.

(If you did not obtain Graph III you could obtain the same comparison by using Figure 13 and the time intervals 0 to 5 minutes, 0 to 2½ minutes and 2½ to 5 minutes, say.)

Our result came from the part of Figure 13 shown in Figure 17.

The result is

$$\begin{aligned}\text{rate at 5 minutes} &= \text{slope of tangent} \\ &= \frac{0.0174 - 0.0145}{2} \\ &= 0.00145 \\ &= 1.45 \times 10^{-3} \text{ mol l}^{-1} \text{ minute}^{-1}.\end{aligned}$$

To express it in seconds, as is more usual, divide by 60, so

$$\begin{aligned}\text{rate} &= \frac{1.45 \times 10^{-3}}{60} \\ \text{rate (5 minutes)} &= 2.41 \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}.\end{aligned}$$

$$\text{rate} = \frac{dc}{dt}$$

c is a product

SHOW D R2
IN R23

Look at Figure 15 (or 16). How would you define the rate of a reaction in terms of the concentration of a reactant?

When the reaction profile obtained shows the concentration of a reactant as in Figure 16, then the slope of the tangent to the curve at any particular time is negative. Because the rate must be a positive number (the reaction is occurring!) and the reactant concentration is decreasing, then the rate is given by

$$\text{rate} = -\frac{dc}{dt}$$

where c is the concentration of a reactant, that is, of a reagent being consumed. For your Home Experiment reaction, the rate will be

$$\text{rate} = +\frac{d[\text{I}_2]}{dt} \quad \text{or}$$

$$\text{rate} = -\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt}$$

You will immediately realize that the rate of the reaction will depend on which reagent you choose to measure. The various possible ways of stating the rate at a particular time are related to each other by the stoichiometry of the reaction in exactly the same way as the methods of stating the extent of the reaction are related to each other (section 11.4.2).

How are the rates as defined by

- (a) the concentration of SO_4^{2-}
- (b) the concentration of I_2
- (c) the concentration of $\text{S}_2\text{O}_8^{2-}$

related?

The measured rates are related as shown by the stoichiometry *only if* the stoichiometry is obeyed.

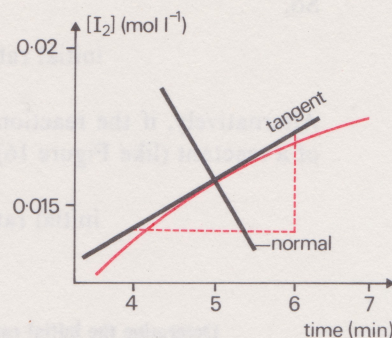


Figure 17 Tangent at 5 minutes on Figure 13.

$$\text{rate} = \frac{dc}{dt}$$

c is a reactant

As shown in section 11.5.2
rate (a) = $2 \times$ rate (b)
and rate (b) = rate (c).

11.4.5 Initial rates

Even though you now know what is meant by the rate of a reaction, you are not much better off because the rate of a reaction, as you can see from your Graph III (or Figure 13), changes continuously throughout the reaction. (Use a ruler to represent the tangent and run it along your curve.) In fact, the rate only looks as if it will stop changing when it becomes zero, that is, when no more reaction is occurring.

Does this mean that the exact conditions and time have to be given every time a reaction rate is mentioned?

Fortunately, the answer is no. One way of giving more useful information than a rate at a particular time is to choose a standard time or extent of reaction. For example, the rate when the reaction was half over (half the reactants consumed) could be given. More useful is the rate when no reactant has been consumed. This is called the *initial rate* of the reaction. It cannot, of course, be measured directly (it is the rate of the reaction when no reaction has occurred!). It can easily be obtained, however, from a graph such as your Graph III, or Figure 13, by determining the slope of the tangent to the reaction profile at zero time.

initial rate

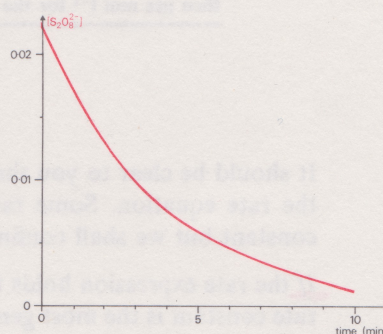


Figure 16 Reactant concentration versus time.

So,

$$\text{initial rate} = + \left(\frac{d[\text{product}]}{dt} \right)_{t=0}$$

Alternatively, if the reaction profile shows the decrease in concentration of a reactant (like Figure 16)

$$\text{initial rate} = - \left(\frac{d[\text{reactant}]}{dt} \right)_{t=0}$$

Determine the initial rate of your reaction from your Graph III.

Your answer will depend on how accurately you are able to draw the tangent at $t = 0$.

Our calculation for Figure 13 went as follows:

$$\begin{aligned} \text{initial rate} &= \frac{0.0198}{4 \times 60} \\ &= 8.25 \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}. \end{aligned}$$

Remember that in measuring the slope it is the length of the triangle you choose, *read from the scale*, that gives the direct result.

11.4.6 The rate equation

From your Home Experiment you will see that the concentration of reactant affects the rate of a reaction; the higher the concentration, the greater the rate.

Stop and think about this for a moment. In the type of reaction we have been considering, what is the first requirement for reaction to occur?

The first condition that must be fulfilled is that the two reacting species should meet. The more reactant molecules in a given volume (concentration), the more collisions will occur.

This establishes that the rate (v) is a function of concentration (c). This statement can be written,

$$v = f(c).$$

The rate of the reaction we have been discussing depends on the concentration of both the reactants. This could be indicated

$$v = f(c_1, c_2).$$

The range of possible functions is very large but the simplest form for this case is

$$v = kc_1c_2.$$

That is, the rate just depends on the product of the two concentrations, k being a constant. This equation is called a rate equation. k is, as you can see, the rate of the reaction when both concentrations are unity. k is called the rate constant for the reaction.

rate equation

rate constant

Work out the dimensions for k for this particular case. First, rearrange the equation to the form

$$k =$$

then use mol l^{-1} for the concentration. (The units of v are in section 11.4.4.)

The equation

$$v = kc_1c_2 \quad \text{becomes}$$

$$k = \frac{v}{c_1c_2},$$

so k is calculated in

$$\frac{\text{mol l}^{-1} \text{ s}^{-1}}{\text{mol l}^{-1} \times \text{mol l}^{-1}}$$

that is,

$$\frac{\text{s}^{-1}}{\text{mol l}^{-1}}$$

$$\text{or } \text{l mol}^{-1} \text{ s}^{-1}.$$

It should be clear to you that the dimensions of k depend on the form of the rate equation. Some rate equations do not even have a single rate constant but we shall confine ourselves to simple expressions.

If the rate expression holds throughout the reaction, then the value of the rate constant is the most general way of describing the rate of the reaction at any particular temperature. Naturally, the value of the rate constant is not much use unless the rate expression is also known.

Using the initial rate that you calculated for your Home Experiment I at the end of section 11.4.5, determine the rate constant for the reaction, assuming that the concentration of iodide remains sensibly constant and that the rate expression is

$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}].$$

You will notice from the last example (if you did not notice earlier) that the dimensions of the rate constant, and of course the units in which it is measured, depend on the form of the rate equation. You have worked these units out for two expressions but clearly there can be many more. The interesting feature of the last example is that the concentration does *not* enter into the units for the rate constant. The rate equation used there is called a *first order** rate equation, because only the first power of concentration is present in the equation.

11.4.7 Summary

We have now dealt with some of the techniques needed to follow a reaction. We have defined the *rate* of a reaction from graphs of concentration of reactants versus time, and concentration of products versus time. You have used such a graph to determine an *initial rate* of a reaction and have seen that if you know the *rate equation* for a reaction you can determine the *rate constant* from such a graph. If you are unsure of any of these terms or procedures look back over sections 11.4 and the answers to the questions.

You should now be in a position to complete the calculations, except for the activation energy, on your Home Experiment for this Unit. For this you will have to complete Unit 12 up to the end of section 12.1.2. You will need these calculations for your Tutor-Marked Assignments on these two Units.

In the next Unit we shall go on to see how the rate constant for a reaction varies with temperature, and what information we can obtain about the reaction at the molecular level from measurements of rates.

For Figure 13 we calculated the initial rate as

$$v_0 = 8.25 \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}.$$

Our initial concentration was

$$[\text{S}_2\text{O}_8^{2-}]_0 = 0.022 \text{ mol l}^{-1}.$$

So because

$$v = kc,$$

$$v_0 = k(c)_0,$$

and hence

$$k = \frac{v_0}{(c)_0}$$

$$= \frac{8.25 \times 10^{-5}}{0.022}$$

$$= \frac{825 \times 10^{-5}}{2.2}.$$

Therefore

$$k = 3.75 \times 10^{-3} \text{ s}^{-1}.$$

* We only include this term because you may meet it in your reading.

Drawing a tangent

Two useful ways of drawing a tangent to a curve are:

- 1 Use a small plane (flat) mirror—place it across the curve at the point where the tangent is required. Arrange the mirror so that the part of the curve in front of the mirror and its reflection in the mirror appear as a continuous curve. This is illustrated in Figure 18. With the mirror in this position draw a line along the line of the mirror—this is the *normal to the curve*. The tangent is a line at right angles to the normal at the point where the normal crosses the curve.

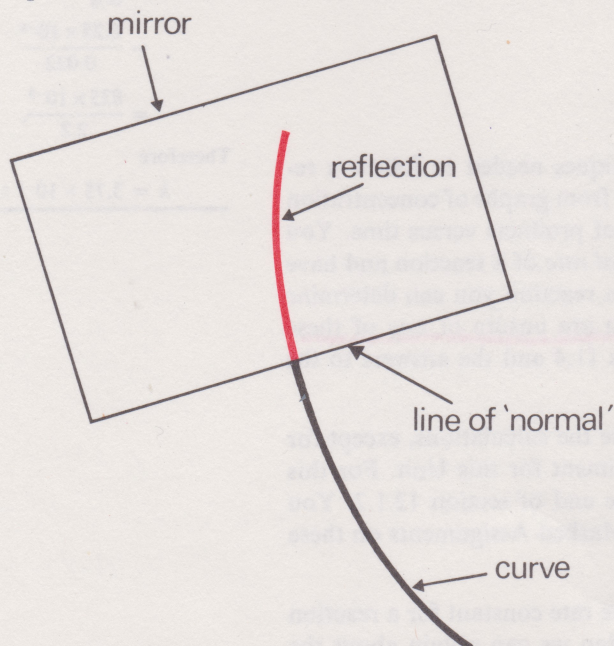


Figure 18 Drawing a tangent with a mirror.

- 2 Use a glass tube or better still a rod. One of your colorimeter tubes would do. It would be even better filled with water and stoppered. Place the tube (or rod) across the curve. Adjust the tube so that the line viewed through the tube is continuous (see Fig. 19). With the tube in the correct position draw a line along the line of the tube—this is the *normal* to the curve and the tangent is at right angles to this.

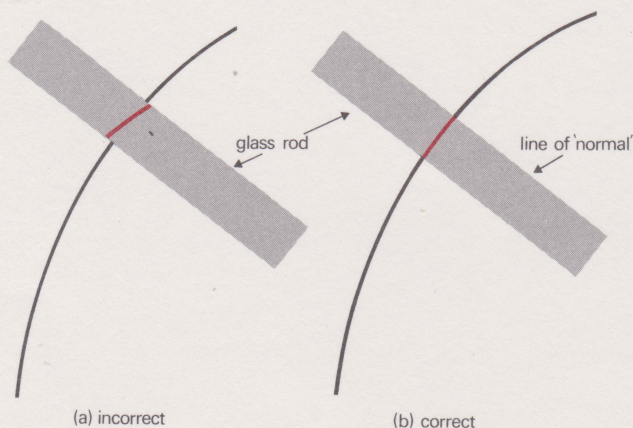


Figure 19 Drawing a tangent with a glass rod or tube.

Appendix 2 (Black)

Combination of chlorine atoms

In the case being discussed, $\text{Cl}_2 \rightarrow 2\text{Cl}\cdot$

$$D(\text{Cl}-\text{Cl}) = 243.46 \text{ kJ mol}^{-1}.$$

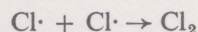
For the reverse process, $\text{Cl}\cdot + \text{Cl}\cdot \rightarrow 2\text{Cl}$, the energy released would be $243.46 \text{ kJ mol}^{-1}$.

How is this energy released? The answer 'as heat' is unsatisfactory in this context because you have seen (Unit 5) that heat is merely one form of energy and so the answer begs the question. A more sensible answer might be, 'by causing the temperature of the gas to rise'.

Again, reference to Unit 5 reminds you that the temperature of a gas is related to the average kinetic energy of the molecules.

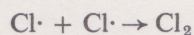
Think about the reaction in molecular terms. Is there any way in which the energy released can turn into kinetic energy, that is, into velocity of the molecule formed?

The molecule could only gain kinetic energy if a force acted on it. It is like the problem of trying to lift yourself by your own bootlaces. It does not matter how strong you are (how much energy you can expend), you cannot succeed. In fact the energy released can only result initially in vibrational energy and clearly the molecule will have $243.46 \text{ kJ mol}^{-1}$ of vibrational energy; this is of course the bond dissociation energy so the bond will break. We can picture what happens in simple terms by referring to the Morse curve (Fig. 2). The inter-action energy of the whole system (the two chlorine atoms) is represented by the curve. Initially in the reaction



the atoms are far apart and the energy of the system is represented by a point on the right hand end of the curve. As the atoms approach each other the separation between the chlorine atoms decreases and the potential energy drops (i.e., is converted to kinetic energy) until the minimum at r_e . The atoms would then overshoot their equilibrium position r_e , and finally come to rest (zero kinetic energy) at a separation such that E is equal to D_0 . They are now in a region of strong interatomic repulsion (that is, closer than r_e) and they will consequently move apart, passing again through the potential energy minimum (r_e). Because they have total energy D_0 , this movement will continue until the atoms fly completely apart again.

Is the reaction



then impossible?

Can you think of any other way in which the molecule can lose some of this energy? Think about Unit 5, section 5.3, and spectra in Unit 6, section 6.4.

There are in fact two ways the molecule *might* lose energy. From Unit 5 you will remember that molecules in a gas continually exchange energy on collision. If our newly formed molecule can collide with another molecule before it has had time to fly apart it could lose some of its vibrational energy and would then be stable. In Unit 6 atoms lost energy by radiating

photons of electromagnetic radiation. If our 'energetic' molecule could emit a photon before it flies apart then it would be stable.

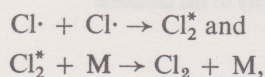
What would determine whether either of these events can happen?

The factor that will determine whether either of these can happen will be time. In the first case the important time is the time between collisions, and in the second it is the time it takes for our molecule to emit a photon. How do these times compare with the times for ONE vibration of the 'energetic' molecule? The relevant times are approximately 10^{-13} s between collisions (depending on pressure), 10^{-7} s to radiate a photon and 10^{-13} s for one vibration.

Is either deactivation process likely to occur?

Yes, collisional deactivation is likely if the pressure is high enough, but radiation is most unlikely.

The reaction is usually written



where the asterisk indicates an 'energetic' molecule and M any molecule that can receive energy on collision.

Unit 12

Section 1

12.0 Introduction

In Unit 11 we dealt with the theoretical ideas of how reactions occur at a molecular level. In this Unit we shall be more concerned with the experimental information that can be obtained about reactions, and shall then try to show how this information can be related to events at the molecular level. We shall continually refer back to the concepts developed in the last Unit.

12.1.1 Effect of temperature on the rate of a reaction

In section 11.3.3 you saw how the energy required for a reaction to take place could result from the fact that molecules have a range of energies. You also saw (for example, Figs. 11 and 12) in qualitative terms that, if those ideas are correct, the rate of a reaction should increase with temperature. In fact when you did the Home Experiment in Unit 11 you saw this for yourself.

Reactions are normally studied over a range of temperatures. A series of typical results is given in Table 1.

temp. (° C)	410	420	430	440	450	460	470	480	490	500
T(K)	683	693	703	713	723	733	743	753	763	773
10 ⁴ × k (s ⁻¹)	0.264	0.483	0.868	1.540	2.685	4.61	7.80	13.0	21.4	34.8

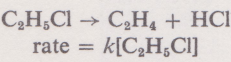


Table 1 Variation of rate constant with temperature.

(Note that it is the rate constant k that is listed rather than initial rates or actual rates. As we have said, this is the most general way of expressing the rate data but it is only *useful* if the rate expression is known, cf. section 11.4.6. Also notice that it is the absolute temperature, T , in kelvin, denoted by K, that is used.)

From the Table you can see that k , the rate constant, increases as the temperature increases and as we said in Unit 11 (section 11.3) the rate approximately doubles for a 10° rise in temperature.

The plot of rate constant, as a function of temperature, for the results in Table 1 is shown in Figure 1.

12.1.2 Form of k versus T

You may have recognized the type of curve that Figure 1 is. It is an exponential curve (see Unit 2, section 2.5.4, and *MAFS*, section 5.C). One way of expressing this particular relationship between k and T is

$$\log k = B - \frac{D}{T} \dots\dots\dots(1)$$

where B and D are constants,

so that if $\log k$ is plotted as a function of $\frac{1}{T}$ a straight line is obtained. This

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graph for the values in Table 1 is shown as Figure 2. The $\log k$ and $\frac{1}{T}$ values are listed in Table 2.

$10^3 \times \frac{1}{T}$	1.464	1.443	1.422	1.403	1.383	1.364	1.346	1.328	1.311	1.294
$\log k$	$\bar{5}.4216$	$\bar{5}.6839$	$\bar{5}.9385$	$\bar{4}.1875$	$\bar{4}.4289$	$\bar{4}.6637$	$\bar{4}.8921$	$\bar{3}.1139$	$\bar{3}.3304$	$\bar{3}.5416$
$\log k$	-4.578	-4.316	-4.062	-3.813	-3.571	-3.336	-3.108	-2.886	-2.670	-2.458

Table 2 Values of $\log k$ and $\frac{1}{T}$.

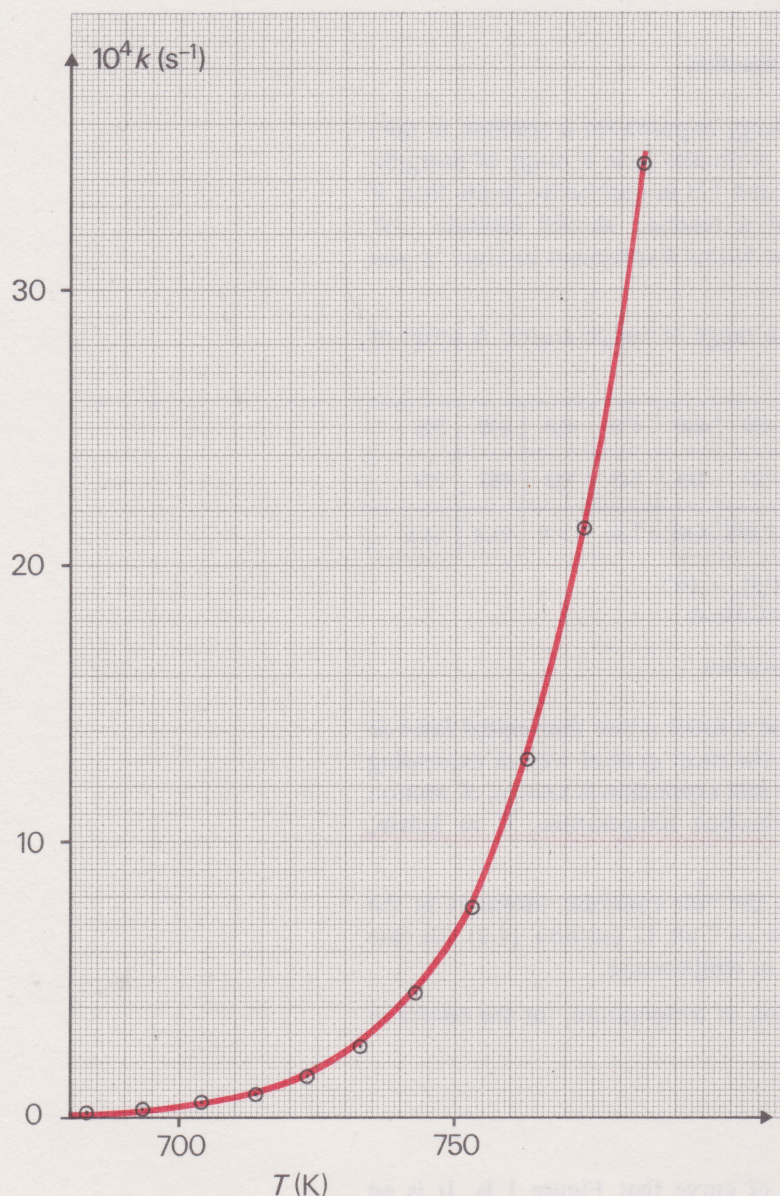


Figure 1 Rate constant versus temperature.

You will notice that this line has a negative slope. Because k increases with temperature, $\log k$ also increases with temperature and so $\log k$ decreases with increasing values of $\frac{1}{T}$. The faster k increases with T the larger will be the (negative) slope of the line in Figure 2.

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17

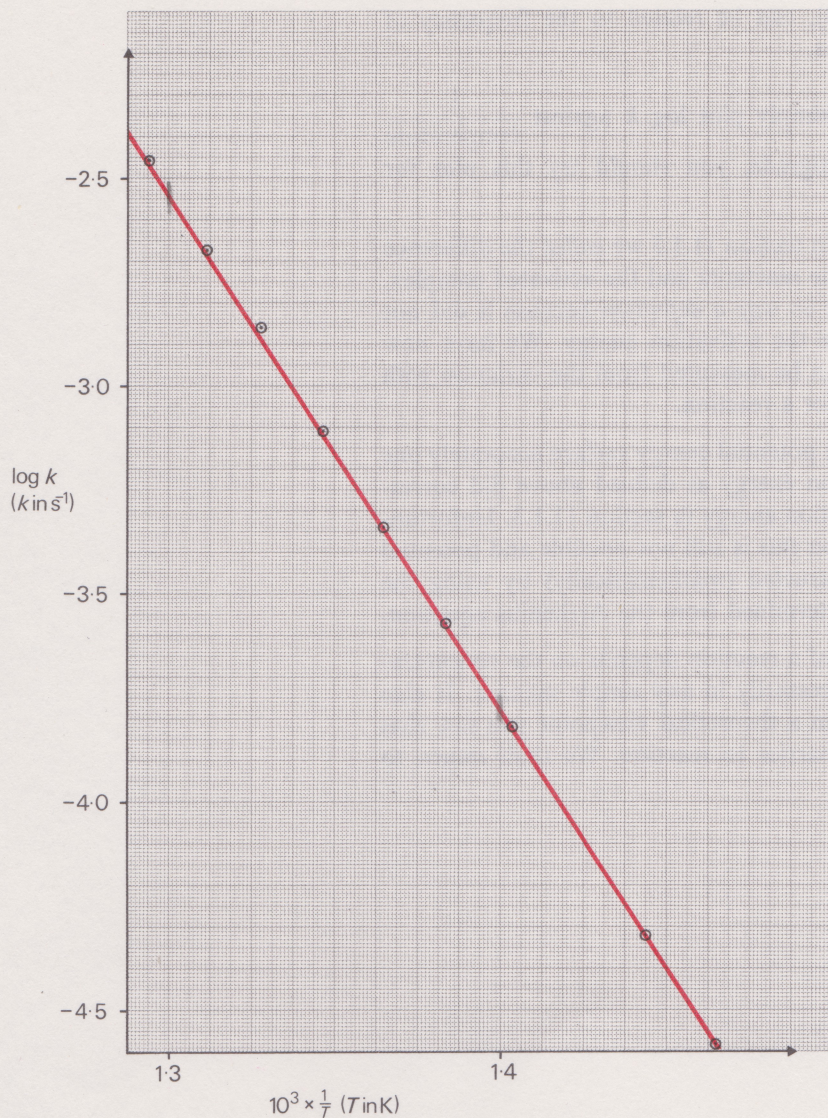


Figure 2 $\log k$ versus $\frac{1}{T}$.

This type of relationship between the rate constant and temperature was first proposed by the Swedish chemist Arrhenius, and equation (1) is one form of the Arrhenius equation. The slope of the line in Figure 2 can be used to define the activation energy (E_A) for the reaction. It is defined* as

$$E_A = 19.143 D \dots\dots\dots(2)$$

where E_A is given in joules per mole (J mol^{-1}).

So the Arrhenius equation can be written

$$\log k = B - \frac{E_A}{19.143 T} \dots\dots\dots(3)$$

Determine the activation energy for the results in Table 1.

* The numerical factor (19.143) arises because the activation energy is defined from the Arrhenius equation expressed in exponential form. The value is $2.3026R$ where R is the gas constant you met in Unit 5, and arises from the Boltzmann distribution (see 11.3.2). The factor 2.3026 is there because equation (3) is expressed in logarithms to the base 10 rather than in natural logarithms (see MAFS sections 1B and 5C).

OBJECTIVE 18

activation energy

One possible calculation, from Figure 2, is

$$\begin{aligned} \text{slope} &= -\frac{3.781 - (-2.532)}{(1.400 - 1.300) \times 10^{-3}} \\ &= -\frac{1.249}{0.100 \times 10^{-3}} \end{aligned}$$

$$\text{so } D = 12.49 \times 10^3.$$

$$\begin{aligned} \text{So } E_A &= 19.143 \times 12.49 \times 10^3 \\ &= 239 \times 10^3 \text{ J mol}^{-1} \\ &= 239 \text{ kJ mol}^{-1}. \end{aligned}$$

Notice that for convenience we chose a simple change in $\frac{1}{T}$ and determined the corresponding change in $\log k$ from the graph.

B, the other term in equation (3), can be related to the frequency of collisions of the reacting molecules.

If you wonder why we did not simply plot $\log k$ against $\frac{1}{\text{temperature}}$ with temperature in degrees centigrade, you should try this plot for yourself.

You might note at this stage that in section 11.1.3 we *called* the difference between the potential energy of the reactants and the activated complex, the activation energy. *This was in no way a definition* because it did not give any idea of how to measure the activation energy. We have now defined it in such a way that it can be measured from the variation with temperature of the rate constant for a reaction.

If it were possible to determine the potential energy surface accurately one could check whether the activation energy as defined above did correspond to the thing we called activation energy in section 11.1.3. Unfortunately, even for the simplest reaction this is still not possible and potential energy surfaces are usually constructed (mathematically) by using the experimental activation energy determined from the Arrhenius equation.

You have now seen that the rate of a reaction depends on the concentrations of the reagents, but not necessarily in any simple manner. It also depends on the temperature. From a theoretical viewpoint you saw that the rate depends on the energy barrier to reaction. We shall return to these questions in section 12.4.2.

12.2.1 The yield of a reaction

In the last few sections we have been discussing the rates of reactions. We now propose to return to the second question posed at the start of Unit 11, 'What is the yield of the reaction?', and see how the concepts developed in Unit 11 apply to yields and whether the yield obtainable is related to the rate of the reaction.

First we need to define the yield of a reaction. The most obvious definition of yield is the one of practical interest, namely, the percentage of reactant converted to product. However, the quotation at the start of Unit 11 will have warned you of the limitations of this practical approach. As implied there, and as discussed in Unit 9 for special cases, there is in fact a theoretical limit to the yield of a reaction. From our point of view in this Unit, it is this limit that is of the most interest because it has a definite value and is related to the concepts we have been using.

From Unit 9 and your Home Experiment for this Unit you will have seen that the most convenient expression for the theoretical limit to the yield of a reaction is the equilibrium constant K . The form K takes is determined by the stoichiometry of the reaction.

For the general reaction



the form of the equilibrium constant is

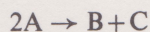
$$K = \frac{(\text{concentration of C}) \times (\text{concentration of D})}{(\text{concentration of A}) \times (\text{concentration of B})}$$

Showing concentrations by the use of square brackets (as in Units 9 and 11), for the general reaction above,

$$K = \frac{[C][D]}{[A][B]} \dots\dots\dots(4)$$

Note that the expression consists of the product concentrations (multiplied together) divided by the reactant concentrations (multiplied together).

The expression for K for other types of reaction can also be written by inspection of the stoichiometry. For example, the equilibrium expression for



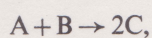
can be obtained by rewriting the equation



when it is obvious that

$$K = \frac{[B][C]}{[A]^2}$$

Similarly, for a reaction of the type



you can rewrite as



so that

$$K = \frac{[C]^2}{[A][B]}$$

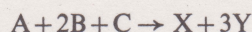
equilibrium constant

0.372512
21/12



0.372512 21/12

For more complex cases the same holds, for example,

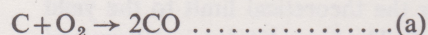


gives as the expression for K

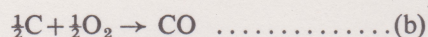
$$K = \frac{[X] [Y]^3}{[A] [B]^2 [C]}$$

Write the expression for K for the reaction performed in the Home Experiment for Unit 11.

If K is constant, then clearly the inverse $\left(\frac{1}{K}\right)$, that is reactant divided by product, must also be constant. In fact, any number multiplied by K , for example, $8K$ will also be constant, as will be the square root of K or K^2 . This can lead to confusion, because the stoichiometry of a reaction can sometimes be written in different ways resulting in different expressions for K . For example, the reaction

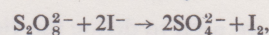


can (correctly) be written



Write the two expressions for the equilibrium constant (K_a and K_b). How are they related?

The stoichiometry is



so

$$K = \frac{[SO_4^{2-}]^2 [I_2]}{[S_2O_8^{2-}] [I^-]^2}$$

12.2.2 An aside

We emphasize here that, while the expression for the equilibrium constant K can be written by inspection of the stoichiometry of the reaction, *this is not true* for the rate constant k . The form of the latter can *only* be obtained by experiment.

The classical illustration of the above is the two gas-reactions

- (a) hydrogen + iodine
- (b) hydrogen + bromine.

The stoichiometries of the reactions are similar:

- (a) $H_2 + I_2 \rightarrow 2HI$
- (b) $H_2 + Br_2 \rightarrow 2HBr$,

so the expressions for the equilibrium constants are

- (a) $K = \frac{[HI]^2}{[H_2] [I_2]}$
- (b) $K = \frac{[HBr]^2}{[H_2] [Br_2]}$.

But experiment has shown that for most conditions the rate expression for reaction (a) is

$$\text{rate} = k [H_2] [I_2]$$

$$K_a = \frac{[CO]^2}{[C] [O_2]}$$

and,

$$K_b = \frac{[CO]}{[C]^{\frac{1}{2}} [O_2]^{\frac{1}{2}}},$$

so that

$$K_a = K_b^2, \text{ but see Appendix 1 for } [C(s)].$$

whereas that for (b) is

$$\text{rate} = \frac{k [\text{H}_2] [\text{Br}_2]^{\frac{1}{2}}}{1 + \frac{[\text{HBr}]}{k' [\text{Br}_2]}}$$

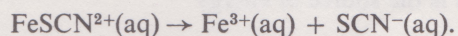
These different rate expressions indicate that the reactions occur by different mechanisms. The hydrogen/bromine reaction consists of a series of reactions. This is an example of the type of reaction mentioned in section 11.4.6 where there is no single rate constant for the reaction.

12.2.3 Dynamic equilibrium

If you look back at the reaction profiles in Unit 11 you will see that the rate of a reaction decreases with time and seems to approach zero. Certainly after a time the rate is very slow and in fact you assumed that it became zero after about 10 half-lives in your Home Experiment for Unit 11.

Does this mean that the reaction has then stopped?

In a reaction that has reached equilibrium the concentration of the reactants no longer decreases, so that from that point of view it *has* stopped. However, try to imagine what is happening at a molecular level. For example, supposing in the Home Experiment for this Unit a ferric ion meets a thiocyanate ion with sufficient energy to react. There is no way that these two ions can 'know' that the reaction is at equilibrium. This being so, the only way that equilibrium can be maintained is if some ferrithiocyanate ions are undergoing the reverse reaction,

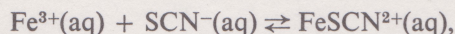


This reverse reaction can, of course, start occurring as soon as there is *any* ferrithiocyanate ion present but because its rate will depend on the concentration of ferrithiocyanate ion it will be very slow to start with, but its rate will increase as the amount of reaction between ferric and thiocyanate ion increases.

At equilibrium the rates of the two reactions must be the same. So it is a *dynamic equilibrium*. At the molecular level both reactions are proceeding, but at the macroscopic level the concentrations are not changing. This is quite unlike the *static equilibrium* of a book on a table (see Unit 3).

dynamic equilibrium

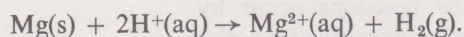
In this case the rate of formation of FeSCN^{2+} by the reaction of Fe^{3+} with SCN^{-} must be exactly equal to the rate of formation of Fe^{3+} from FeSCN^{2+} . The reaction could therefore more sensibly be written



where the double arrow indicates reaction occurring in both directions. The reaction of ferric ions can be referred to as the *forward reaction* in this case and the reaction of ferrithiocyanate to form ferric ion as the *reverse reaction*. So in this sense the reaction has not stopped even though it has reached equilibrium.

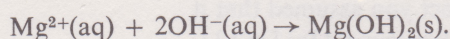
12.2.4 Do all reactions have an equilibrium constant?

Most of the reactions you performed in the Home Experiment for Unit 9 were represented by an equation that showed reactants turning into products. For example,

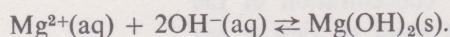


Does this reaction have an equilibrium constant? This is not an easy question to answer with the information you have available. Doing the reaction the way you did, in an open test tube, one of the products (H_2) is removed from the reaction environment, so is not present to take part in the reverse reaction.

Another reaction you performed in Unit 9 was the precipitation of magnesium hydroxide

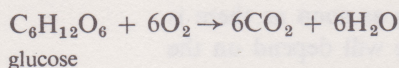


Here the question 'Is there an equilibrium constant?' was in fact answered in Unit 9. If magnesium hydroxide is shaken with water a small amount of it dissolves and there are *some* magnesium and hydroxide ions in the solution, so the precipitation reaction *could* correctly be written



However, the amount of magnesium ion left at equilibrium is so small that the equilibrium constant is very large (see Appendix 1, Black).

In spite of the fact that most reactions you deal with, to all intents and purposes, go to 'completion' there is still an equilibrium constant but its value is very large. For example, one of the important reactions in biological systems is the oxidation of glucose. This is the source of energy for most biological processes (see Unit 15).



This reaction has an equilibrium constant at room temperature of about 10^{500} —an enormous number indeed.

You will wonder how we can possibly get a value for such an equilibrium constant. Certainly not by the type of chemical analysis that you have performed in your Home Experiment for this Unit. A clue as to how this value is obtained will be found later in this Unit (section 12.4). The point we have made here is that all reactions do have an equilibrium constant.

12.2.5 Activities

At high concentrations the value of the equilibrium constant as defined above is no longer a constant. There are good theoretical reasons for this, associated with the fact that at high concentrations each solute molecule or ion is no longer surrounded entirely by solvent molecules but is influenced by other solute molecules.

The equilibrium constants in the expressions written above are only constant if *activities* are used instead of concentrations. You may regard activities as effective concentrations. We do not propose to deal with activities in the Foundation Course but shall continue to use concentrations. We only include this section in case you meet the concept of activity in your reading.

activities

12.3.1 Variation of the equilibrium constant with temperature

From your Home Experiment you will realize that the equilibrium constant for a reaction varies with temperature. You found that the rate of a reaction increases with increase in temperature, and on this basis you might expect the maximum theoretical yield of a reaction similarly to increase, that is, for the equilibrium constant to increase with increase in temperature. However, you should now have your doubts about this. Most reactions that occur readily at room temperature have a value of the equilibrium constant that decreases with increase in temperature, that is, less product is formed at higher temperatures.

You might guess that the way the equilibrium constant varies with temperature is in an exponential manner and that a plot of $\log K$ against $\frac{1}{T}$ would be a straight line. This is approximately true, particularly for limited ranges of temperature. However, as indicated above, the equilibrium constant for some reactions increases with temperature and for others it decreases with temperature. The slope of a graph of $\log K$ against $\frac{1}{T}$ can be either positive or negative.

What was the sign of the slope of $\log K$ versus $\frac{1}{T}$ for your Home Experiment for this Unit?

By analogy with the variation of the rate constant with temperature, you might expect that the slope of the $\log K$ versus $\frac{1}{T}$ plot is related to an energy change. In fact, the relationship is with the enthalpy change for the reaction.

If we write the variation of K with $\frac{1}{T}$ as

$$\log K = L - \frac{M}{T}$$

the slope of the line ($-M$) is related to ΔH° , the standard enthalpy change for the reaction by

$$\begin{aligned}\Delta H^\circ &= -\text{slope} \times 19.143 \\ &= 19.143 M.\end{aligned}$$

Calculate the standard enthalpy change for your Home Experiment reaction.

So the variation of the equilibrium constant temperature can be written

$$\log K = L - \frac{\Delta H^\circ}{19.143 T} \dots\dots\dots(5)$$

where, as before, T is in kelvin (K).

The resemblance between this equation and equation (3) is obvious. However, over wide temperature ranges there is experimental evidence that both L and ΔH° can vary with temperature, and the theoretical reasons for this are well understood but will not be dealt with in the

If you found K increasing with increasing temperature then $\log K$ will also increase with temperature and so will *decrease* with an increase of $\frac{1}{T}$. So the slope is negative. If you found K decreasing with temperature the reverse is true.

As an example, if the two values of K and T were as given in Table 3, we would have completed the table as shown (see p. 48).

Foundation Course. We shall have a little more to say about the term L in equation (5) later (section 12.4.1).

12.3.2 Summary

This is an appropriate point to summarize the information you have about reactions so far. From a theoretical point of view you have seen that there is an energy barrier to reaction that has to be overcome before reaction can occur, and that there is an overall energy change for a reaction, but that these two things are not directly related. (Though each can set a limit on the size of the other in some circumstances.) Then you have seen that the rate of a reaction varies with temperature and that from this variation you can obtain the value for the activation energy (E_A), which in Unit 11 we called the energy barrier to reaction. Similarly you saw that a reaction has a theoretical maximum yield which can conveniently be expressed by an equilibrium constant. The variation of the equilibrium constant with temperature gives a value for the standard enthalpy change ($\Delta H^\ominus$) for the reaction. In Unit 11 you represented both E_A and $\Delta H^\ominus$ on a reaction co-ordinate. We now go on to draw some implications from this knowledge. You can probably anticipate most of them.

p15, 18, 19.

temperature ($^\circ\text{C}$)	20	40
K	21	1.5
$T(\text{K})$	293	313
$10^3 \times \frac{1}{T}$	3.41	3.19
$\log K$	1.32	0.18

Table 3 Equilibrium constants at different temperatures.

You could, of course, plot these two results but it is more sensible to get the slope simply from:

Slope = $\frac{\text{change in } \log K}{\text{change in } \frac{1}{T}}$

$$= \frac{0.18 - 1.32}{(3.19 - 3.41) \times 10^{-3}}$$
$$= + 5.64 \times 10^3$$

$\Delta H^\ominus = -108 \text{ kJ mol}^{-1}.$

12.4.1 The equilibrium constant and the enthalpy change for a reaction

In section 11.2.4 the enthalpy change for a reaction was related to the dissociation energies of the bonds being broken and formed in the reaction. (Though we warned of the dangers of ignoring the interactions of the solvent molecules in reactions in solutions in section 11.2.1.)

Will the equilibrium constant for the reaction in Table 1 increase or decrease with temperature? Use the bond energies in Table 4.

D(C–Cl) 339	D(C–C) 346
D(C–H) 410	D(C=C) 610
D(H–Cl) 432	

Table 4 Bond dissociation energies in kJ mol^{-1}

There is one immediate implication of the relation between the equilibrium constant and the standard enthalpy change. Because ΔH° depends only on the stoichiometry of the reaction (not on how that stoichiometry is achieved, see 12.4.2) there is one and only one value of ΔH° . That the relationship of the equilibrium constant is with the standard enthalpy change makes this clear. This means that the only way to change the value of the equilibrium constant is to change the temperature.* However, as you will hear in the radio programme with this Unit, even when the equilibrium constant is fixed by keeping the temperature constant, the *yield* can be changed but this is implicit in the various formulae for the equilibrium constant. For example, in equation (4) the theoretical yield of D (say) can be increased by increasing the concentration of A present.

Will doubling the concentration of A in equation (4) double the yield of D?

The way the equilibrium constant varies with temperature depends on the sign of ΔH° . This can be regarded as an example of Le Chatelier's principle (see Unit 9, section 9.20). If a reaction is endothermic (ΔH° is positive) heat is absorbed, so the reaction is favoured if more heat is available. This means that the equilibrium constant will increase if the temperature increases, more product being formed. The reverse is true if the reaction is exothermic (ΔH° is negative), an increase in temperature resulting in a decrease in K .

Most of the reactions that you have carried out have been exothermic, so ΔH is negative and the equilibrium constant is positive (in most cases very large). So the sign of ΔH° not only determines the way the equilibrium constant changes with temperature but also influences the size

* This is not strictly always true because there are ways of changing the activities (section 12.2.5) of substances without changing the temperature, but we are ignoring these complications here.

By the reasoning in section 11.1.4

ΔH = dissociation energies of bonds broken – dissociation energies of bonds formed

$$= \text{D(C–Cl)} + \text{D(C–H)} - \text{D(H–Cl)} - \text{X}$$

where X is the difference between D(C=C) and D(C–C) .

$$\begin{aligned} \Delta H &= 410 + 339 - 432 - 264 \\ &= +53 \text{ kJ mol}^{-1}, \end{aligned}$$

that is, ΔH is positive (the reaction is endothermic) so K increases with increasing temperature. Bond dissociation energies like those in Table 4 are more likely to have been obtained from heats of reaction than vice versa.

Not necessarily. To keep K constant all that is necessary is that the product of $[C]$ and $[D]$ should double. Both concentrations could increase by a factor of the square root of 2, but $[B]$ will also change, so the effect on $[D]$ is not immediately obvious.

0.375
23

of the equilibrium constant. Often if ΔH° is negative the equilibrium constant is large and the reaction goes nearly to 'completion'. However, you have seen some examples of reactions that are endothermic but nevertheless occur quite readily at room temperature. The value of the equilibrium constant in these cases clearly is determined in part by the value of the term L in equation (5). This term is related to the *entropy change* for the reaction. You have met entropy in Unit 5 but we do not propose to discuss it further here, except to point out that there are two factors affecting the value of the equilibrium constant for a reaction. One is the standard enthalpy change, which can be interpreted in terms of bond energies, and the other is the standard entropy change. It is the former that determines how the equilibrium constant changes with temperature, but clearly from equation (5) the entropy change will become relatively more important at high temperatures when the term involving T becomes smaller.

12.4.2 The rate of a reaction and the activation energy

In contrast with the equilibrium constant the rate of a reaction (and hence the rate constant) depends on *how* the stoichiometry of a reaction is achieved. That is, it depends on the *mechanism* of the reaction. You have already seen in Unit 11 two ways in which a simple reaction can occur, and you also saw that the energy barrier to reaction is not determined by the dissociation energies of the bonds being broken or formed. Though the former usually sets a limit to E_A .

A reaction will go faster if a mechanism involving a lower activation energy can be found. This can sometimes be achieved by performing the reaction in the presence of a *catalyst*, a substance that assists the reaction, usually without itself being consumed. The study of *catalysis* is almost a subject in itself and the types of catalyst vary enormously. Later (Units 14 onwards), we shall examine some of the important biological catalysts that you met in Unit 10—enzymes. These are very efficient (and very specific) catalysts but normally only function at a limited range of temperatures.

Some catalysts act by forming an intermediate compound with one of the reactants. This later reacts to form the products.

Write a general mechanism for such a catalyst (G, say) for the reaction $A+B \rightarrow C+D$.

mechanism

catalyst
catalysis

Objective 26

Assuming that the intermediate is formed with A, the first step might be:
 $A+G \rightarrow AG$ followed by
 $AG+B \rightarrow C+D+G$.

You met this type of sequence in Unit 10, section 10.5.5.

There are many variations of this type of mechanism. Another way that catalysts can function is to absorb one or more of the reactants (on a surface, say) so that they can react more readily, for example, the combination reaction of A and B to form A-B.

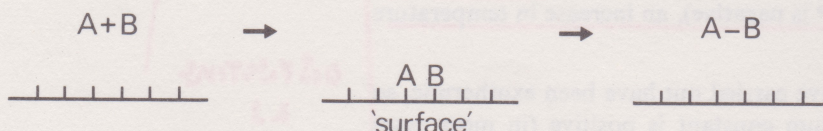


Figure 3 Surface catalysis.

The above two types of catalytic action are related and no clear distinction can be drawn between them.

It should be clear from section 12.4.1 that the role of a catalyst is to increase the rate of a reaction but that it *cannot* alter the value of the equilibrium constant for the reaction. If a catalyst is present at equilibrium, then it follows that *both* the forward and reverse reactions must have their rates increased. In increasing the rate of a reaction, the catalyst usually changes the mechanism and alters the rate equation.

12.5 Requirements for reaction to occur

You now have, in general terms, most of the factors that influence a chemical reaction.

Try listing the requirements for reaction before you read further.

For a reaction to occur:

- 1 the reactant molecules (if there are more than one) must meet (collide);
- 2 the molecules must meet with sufficient energy to react;
- 3 the equilibrium constant must be sufficiently large to *allow* enough reaction to occur for it to be detected.

Requirement (1) is clearly affected by concentration. The more molecules in a given space the more likely they are to meet.

Requirement (2) depends on the mechanism(s) available to the reactants and, of course, on the temperature.

Requirement (3) cannot be altered at a given temperature.

Increasing concentration of the reactants increases the chance of requirement (1) being met and also, in some cases, increases the chance of reaction through requirement (3).

Increasing temperature increases the chance of reaction by meeting requirement (2) but may decrease it through (3).

A catalyst assists by decreasing requirement (2).

The effects of increasing temperature on requirements (2) and (3) often work in opposite directions. An example of this, the industrial production of ammonia by the Haber process, is discussed in the radio programme for this Unit.

12.6 Other types of reaction

We should not leave this topic without a brief mention of some other types of reaction. The reactions we have dealt with so far have depended on obtaining the energy for reaction from collisions between molecules at the high energy end of the Boltzmann distribution (section 11.3.3), and this results in the rate varying with temperature in the way indicated by the Arrhenius equation (section 12.1.2). In some reactions one of the requirements (1)–(3) listed in the last section plays an insignificant role in determining the rate.

Can you suggest some of the reactions that you have performed that fit this description? Which requirement does not seem to be important?

Many reactions between ions in solution appear to have little or no activation energy. So reaction occurs on *every* collision of the reactant ions. In the television programme for this Unit you will see that the rates of these reactions can be measured, but, from what we have just

The reaction you performed in your Home Experiment for this unit and most of the reactions you performed in the Home Experiment for Unit 9 seemed to occur instantaneously. These were all reactions between ions in solution and appear to occur every time the ions meet, so requirement (2) does not seem to be important.

said, the rate of the reaction is largely determined by the speed with which the reactants can come together. This is affected by temperature but not necessarily in the way given in the Arrhenius equation. Other influences will be the concentrations of the reactants and the ease with which the reacting molecules or ions can move through the solution. The latter will depend on the size of the ions, among other things.

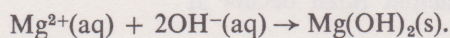
Other reactions that have no (or very little) activation energy are reactions between atoms or free radicals where again reaction often occurs at every collision of the two reactant species.

Another general way in which reactions can differ from those we have been discussing so far is if requirement (2) (the energy for reaction) is met in other ways. Units 6 and 7 will give you a hint as to one possible source of energy. Reactions that obtain their energy by one of the reactants absorbing radiation (when $E = hf$) are called *photochemical* reactions. Photosynthesis is one important biological example of this type of reaction.

photochemical reaction

K for a reaction with a solid product

The reaction discussed in the text is



The form of the equilibrium constant should be

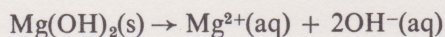
$$\frac{[\text{Mg}(\text{OH})_2]}{[\text{Mg}^{2+}] [\text{OH}^{-}]^2}$$

What is the meaning of the concentration of magnesium hydroxide *in the solution*? This is treated by arbitrarily assuming that the 'activity' is unity and, for our purposes, using the value 1 for the concentration of magnesium hydroxide. This, of course, in no way implies that the concentration of magnesium hydroxide is 1 mole per litre. What is being said is that the solid in contact with the solution has a constant effect *irrespective* of how much solid there is (*provided there is some*), so an arbitrary constant is introduced in the expression for the equilibrium constant and this is taken for convenience as unity.

So

$$K = \frac{1}{[\text{Mg}^{2+}] [\text{OH}^{-}]^2}$$

You will see the relationship with the solubility product if you read Appendix 1 of Unit 9. The reaction is merely written down the other way round.



so

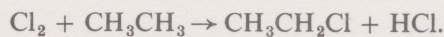
$$K = \frac{[\text{Mg}^{2+}] [\text{OH}^{-}]^2}{1}$$

with the (1) usually omitted.

Section 11.2

Question 1 (Objective 1)

List the bonds broken and formed in the reaction



Question 2 (Objective 2)

For a reaction $\Delta H^\circ = -130 \text{ kJ mol}^{-1}$

Which of the following statements are true?

- (a) the reaction is exothermic;
- (b) the reaction is endothermic;
- (c) the reaction is thermoneutral;
- (d) heat is evolved during the reaction;
- (e) heat is absorbed during the reaction.

Question 3 (Objective 1)

Write the equations that show homolytic bond fission and heterolytic bond fission of HCl. Are the reactions endothermic, exothermic or thermoneutral?

Question 4 (Objectives 4 and 5)

Can

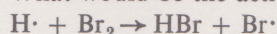
- (a) $E_A < \Delta H$?
- (b) $E_A < |\Delta H|$?
- (c) $E_A = \Delta H$?

(see *MAFS* 1.C.4 and glossary)

illustrate your answers by sketching reaction co-ordinates.

Question 5 (Objectives 1, 2, 3, 4, 5, 6)

- (a) What would be the activated complex for the following reaction?



- (b) Will the separations of the atoms in the activated complex be the same?
- (c) Given that $D(\text{Br}-\text{Br}) = 193 \text{ kJ mol}^{-1}$
 $D(\text{H}-\text{Br}) = 366 \text{ kJ mol}^{-1}$.

What is the heat of the reaction?

- (d) Sketch the reaction co-ordinate, and show ΔH and E_A on your sketch.
- (e) What is the value of the activation energy for the reaction?
- (f) Is the reaction endothermic or exothermic?

Section 11.3

Question 6 (Objective 1)

Write equations whose heats of reaction are the (standard) heats of formation at 298 K for

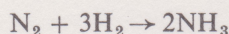
HCl(g), Cl₂(g), H₂O(l), CO(g), CO₂(g),
1, chloropropane (CH₃CH₂CH₂Cl) and
propan-1-ol (CH₃CH₂CH₂OH).

Question 7 (Objective 1)

The (standard) heats of combustion (complete oxidation) of carbon (graphite) and carbon monoxide (gas) are -393.5 and -283.0 kJ mol⁻¹ respectively. What is the standard heat of formation of carbon monoxide?

Section 11.5

Question 8 (Objective 13)



Write three expressions for the rate of the above reaction and show the relationship between them.

Question 9 (Objective 11)

Which of the following is the fastest rate for a reaction?

- (a) the average rate up to 50 per cent reaction;
- (b) the initial rate;
- (c) the rate at 50 per cent reaction.

Question 10 (Objectives 1, 10)

Sketch a reaction profile for a reactant. What additional information would be required to enable you to calculate a rate constant from such a profile?

Section 12.1

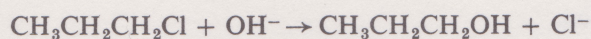
Question 11 (Objectives 18, 19)

It follows from the Arrhenius equation that a graph of $\log k$ versus $\frac{1}{T}$ is a straight line.

- (a) What assumptions are implied by that statement?
- (b) Can you think of a reason for the equation containing T rather than the temperature in °C (see section 11.3.2 and the reference there to Unit 5)?

Section 12.2

Question 12 (Objectives 1, 20)



How can the yield of propan-1-ol, expressed as a percentage of the 1, chloropropane used, be increased at a given temperature?

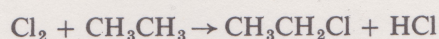
Section 12.3

Question 13 (Objective 23)

Answer question 12 for the circumstances in which the temperature can be varied (section 11.2.2 might help).

Section 12.4

Question 14 (Objectives 1, 3, 15, 23)



given

$$\text{D}(\text{Cl}-\text{Cl}) = 243$$

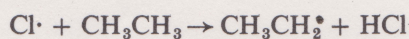
$$\text{D}(\text{CH}_3\text{CH}_2-\text{H}) = 410$$

$$\text{D}(\text{CH}_3\text{CH}_2-\text{Cl}) = 339$$

$$\text{D}(\text{H}-\text{Cl}) = 432$$

all in kJ mol^{-1}

- How will the equilibrium constant for this reaction vary with temperature?
- Could you answer the question if you had been given the heterolytic bond dissociation energies?
- Write one possible rate equation for the reaction.
- If one step in the reaction is



draw a possible activated complex for this step.

Question 15 (Objectives 1, 22)

The equation

$$\log K = L - \frac{\Delta H^\circ}{19.143T}$$

can be used to determine ΔH° for a reaction.

- (a) What restrictions apply to *this* use of the equation?
- (b) If these restrictions are met ΔH° can be obtained by plotting $\log K$ versus $\frac{1}{T}$, drawing the best straight line through the points and determining the slope of the line. What assumption does this procedure make?
- (c) State another purpose for which this equation can be used (examine your answer to (a)).

Self-Assessment Answers and Comments

Question 1

Bonds broken	Cl – Cl C – H
Bonds formed	C – Cl H – Cl

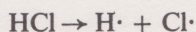
Question 2

(a) and (d) are true.

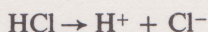
The enthalpy change in a reaction is given by the sum of the enthalpies of the products less the enthalpies of the reactants. If the sum of the enthalpies of the products is less than that of the reactants ΔH will be negative. But by the Law of Conservation of Energy the enthalpy lost must go somewhere and it results in heat being evolved.

Question 3

Homolytic bond fission

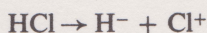


heterolytic bond fission

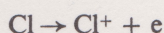


Both reactions are endothermic (require energy).

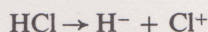
The question may occur to you: 'Why cannot heterolytic fission be shown as follows?'



You have dealt with the process:



Do you recall what the energy for this reaction is called? You met the process in Units 6 and 7. (The answer is in brackets below the comment on question 4). It is also possible to form an H^- ion. Therefore the reaction



should be possible. The reason that heterolytic fission is not written this way is that the other reaction requires less energy and so is more likely to occur.

Question 4

(a) No (b) Yes (c) Yes

The activation energy of a reaction (as we have treated it in these Units) must be positive so it cannot be less than ΔH , the reaction co-ordinate for answer (c) makes this clear. For (b) to be true only requires a strongly exothermic reaction with a small activation energy as in Figure 4.

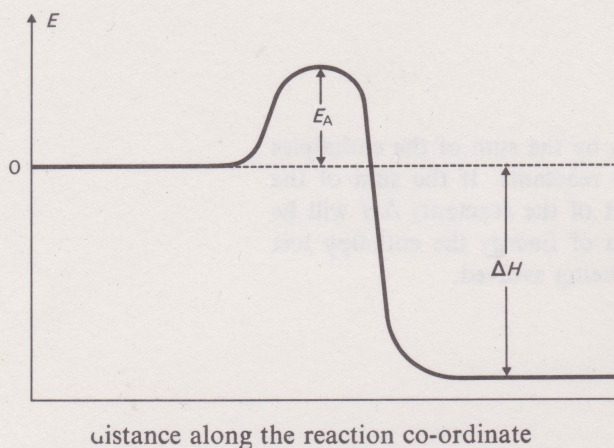
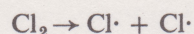


Figure 4 $E_A < |\Delta H|$.

For a simple bond breaking reaction, say:



the reaction co-ordinate would be as shown in Figure 5.

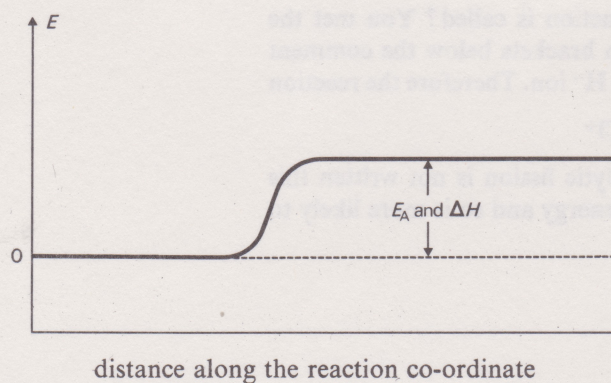


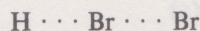
Figure 5 $E_A = \Delta H$.

You can see this from an examination of the Morse curve (Unit 11, Fig. 2).

(The energy in question 3 is the ionization energy of a chlorine atom.)

Question 5

(a) Activated complex

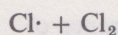


(b) The H/Br and Br/Br distances will *not* be the same. Think of the number of electrons surrounding each nucleus.

(c) $\Delta H = \text{Energy of bond broken} - \text{energy of bond formed}$
 $= 193 - 366$
 $= -173 \text{ kJ mol}^{-1}$.

(d) The reaction co-ordinate will look like Figure 8 in Unit 11.

(e) This question cannot be answered from the information given. From Figure 6 (Unit 11) and the television programme for Unit 11 you could place an upper limit to E_A . This would be $D(\text{Br}-\text{Br})$. That is 193 kJ mol^{-1} . However the corresponding values for

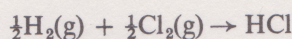


given in section 11.2.3 suggest that the activation energy may be well below this upper limit.

(f) As ΔH is negative the reaction is exothermic.

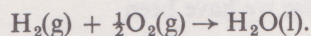
Question 6

Standard heats of formation are the heats of the reactions forming the compounds from their elements, all substances being in their standard states. The reactions are

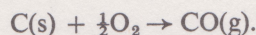


notice that the stoichiometry is arranged so as to form one mole of the compound.

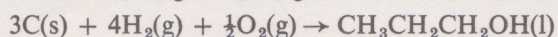
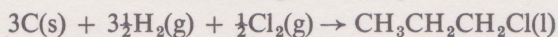
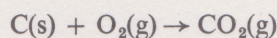
$\text{Cl}_2(\text{g})$ has a zero heat of formation (see section 11.3.3)



A different enthalpy change would result if the product were $\text{H}_2\text{O}(\text{g})$ but as liquid water is the standard state at 298 K (25° C) that enthalpy change is *not* ΔH°



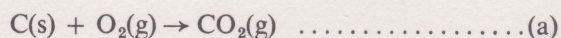
The standard state for carbon is graphite and a different value for ΔH results if diamond is used.



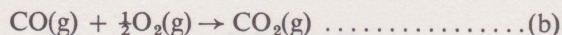
You were not expected to know that these products are liquids at 298 K.

Question 7

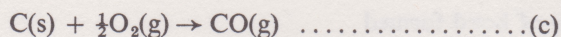
The combustion reactions are



and



whereas the heat of formation of CO(g) is the heat of the reaction



From the Law of Conservation of Energy the change in energy in reaction (a) must be the same as the sum of the energy changes in (c) and (b).

It follows that

$$\begin{aligned}\Delta H_f^\circ; \text{CO(g)} &= -393.5 - (-283.0) \\ &= -110.5 \text{ kJ mol}^{-1}.\end{aligned}$$

Question 8

The rate of the reaction can be given in terms of the disappearance of nitrogen or hydrogen or in terms of the appearance of ammonia. The three expressions are

$$-\frac{d[\text{N}_2]}{dt}, \quad -\frac{d[\text{H}_2]}{dt}, \quad +\frac{d[\text{NH}_3]}{dt}$$

From the stoichiometry of the reaction three hydrogen molecules react for every nitrogen molecule that is consumed and result in two ammonia molecules. Therefore

$$-\frac{d[\text{N}_2]}{dt} = -3\frac{d[\text{H}_2]}{dt} = +2\frac{d[\text{NH}_3]}{dt}$$

Question 9

(b) is correct, but see below.

For the types of reaction profile that you have been considering, for example Figure 13 (Unit 11), the initial rate is the fastest rate of the reaction and the rate decreases as the reaction proceeds. The average rate up to any particular time will have a value between the initial rate and the rate at that time.

However, reaction profiles can be more complex than those we have been considering. A fairly common type is shown in Figure 6.

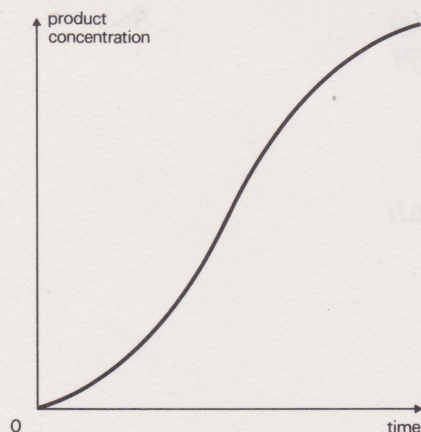


Figure 6 A reaction with a slow start.

This reaction has a slow start, then the rate builds up to a maximum before following the more usual decrease as the reaction proceeds. This type of reaction will almost invariably have a complicated rate equation (see 11.4.6).

Question 10

Your sketch should look like Figure 16 (Unit 11), showing the concentration of reactant decreasing with time. Such a graph would enable you to calculate rates of the reaction at various times (including $t = 0$), but you would require the *rate equation* to enable you to calculate a rate constant.

Question 11

(a) The Arrhenius equation can be written

$$\log k = B - \frac{E_A}{19.143 T}$$

(equation 3, section 12.1.2). A graph of $\log k$ versus $\frac{1}{T}$ is a straight line if:

- ✓ (i) the Arrhenius equation is obeyed;
 - ✓ (ii) B and E_A do not vary with temperature.
- (b) In Unit 5 you saw that T is related to the mean kinetic energy of an ideal gas. In section 11.3.1 we said that one source of energy for reactions was the kinetic energy of the reacting molecules. Clearly at 0°C gas molecules do not have zero kinetic energy.

Question 12

The expression for the equilibrium constant for the reaction is:

$$K = \frac{[\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}][\text{Cl}^-]}{[\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}][\text{OH}^-]}$$

The yield (concentration at equilibrium) of propan-1-ol will increase if either of the reactant concentrations increases. To increase $[\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}]$ as a percentage of $[\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}]$ requires that the other reactant concentration $[\text{OH}^-]$ be increased. Changing one concentration invariably changes others so that K remains constant (but see 12.2.5)

Question 13

In section 11.2.2 you calculated the enthalpy change for this reaction. It is $+125 \text{ kJ mol}^{-1}$. The reaction is endothermic and as indicated in section 12.3.1 the equilibrium constant will increase with increasing temperature. So, a larger yield of propan-1-ol can be obtained by increasing the temperature.

Question 14

- (a) From section 11.2.2 and Question 1

$$\begin{aligned}\Delta H &= D(\text{Cl}-\text{Cl}) + D(\text{CH}_3\text{CH}_2-\text{H}) - D(\text{CH}_3\text{CH}_2-\text{Cl}) - D(\text{H}-\text{Cl}) \\ &= 243 + 410 - 339 - 432 \\ &= -118 \text{ kJ mol}^{-1}.\end{aligned}$$

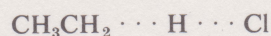
So the reaction is exothermic. From section 12.4.1 K will decrease as T increases.

- (b) Yes. From the Law of Conservation of Energy the *overall* energy change will be the same whether the bonds are broken homolytically or heterolytically. ΔH must be the same in both cases.
- (c) The number of possible rate equations is almost unlimited (see 12.2.2). The simplest would be

$$\text{rate} = k [\text{Cl}_2] [\text{CH}_3\text{CH}_3]$$

but if the suggestion in (d) is correct this rate equation is not likely to apply.

- (d) The probable activated complex would be:



Question 15

- (a) To be able to use the equation to determine ΔH° requires that K can be determined experimentally. This limits the range of values that K could have. It must not be too small or too large. Even a value of 10^4 (say) would not be easy to determine by measuring concentrations.
- (b) See the answers to Question 11 (a), similar considerations apply here.
- (c) If ΔH° can be determined (by experiment or from ΔH_f° values) then the equation can be used to determine K if L is known (or can be calculated or estimated).

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